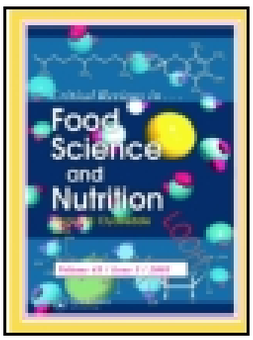

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# Application of nanotechnology based-biosensors in analysis of wine compounds and control of wine quality and safety: A critical review

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**ABSTRACT**

Nanotechnology is one of the most promising future technologies for the food industry. Some of its applications have already been introduced in analytical techniques and food packaging technologies. This review summarizes existing knowledge about the implementation of nanotechnology in wine laboratory procedures. The focus is mainly on recent advancements in the design and development of nanomaterial-based sensors for wine compounds analysis and assessing wine safety. Nanotechnological approaches could be useful in the wine production process, to simplify wine analysis methods, and to improve the quality and safety of the final product.

**KEYWORDS**

Biosensor; enology; nanomaterials; nanoparticles; polyphenols; quality; safety; wine

## Introduction

Nanotechnology has become one of the most promising technologies that have led to a substantial breakthrough in conventional nutrition and food science (Weiss, Takhistov, and McClements 2006). Nanotechnology seems to have a great impact on many areas of the food industry (Adányi et al. 2018; Dumitriu et al. 2018; He and Hwang 2016; Magro et al. 2016; Niaz et al. 2018; Pinilla, Noreña, and Brandelli 2017; Rashidi and Khosravi-Darani 2011; Rodríguez-Delgado et al. 2015; Topuz et al. 2016; Valdés et al. 2009; Zhang et al. 2018), from the development of novel food packing materials to nano-delivery systems, including the analytical control of the whole food chain. An increasingly urgent need for rapid, reliable, and accurate information on the quality and security of foodstuffs has led to the development of more selective and sensitive analytical methods. The use of nanotechnology is one way to achieve this goal (Duncan 2011; Chun, 2009; Oh et al. 2017; Peng et al. 2018; Valdés et al. 2009). Nanotechnology is playing an increasingly important role in the development of biosensors (Jianrong et al. 2004; Kwon et al. 2018; Li et al. 2013). The use of nanomaterials in the development of sensors and in the construction of analytical instruments used in the food industry has increased greatly in recent years. Nanomaterial-based sensing approaches include the use of nanoparticles (NPs) and other nanostructures to enhance sensitivity and selectivity of detection as well as enabling an easier sample preparation. Moreover, they can increase the portability of analytical instruments (Bülbül, Hayat, and Andreescu 2015). In the food industry, the nanotechnological approach can be applied to enhance food quality (Dumitriu et al. 2018; Sozer and Kokini 2009), safety, shelf life, cost, nutritional benefits (Sozer and Kokini 2009), taste characteristics (Duncan 2011), and food packaging (Duncan, 2011; Vilarinho et al. 2018). Also, nanotechnology may be useful for the delivery of natural antimicrobials in food (Pinilla, Noreña, and Brandelli 2017).

One of the most widespread applications of nanotechnology in the field of enology is the chemical analysis of wine which ensures wine quality and safety (Monge and Moreno-Arribas, 2016). Microbial control and wine chemical composition are crucial aspects of wine quality (Bokulich et al. 2016). The analytical equipment implementing nanomaterials can enhance performance and simplify the analysis methodology (Grumezescu 2016). The possible use of nanotechnology in grapevine cultivation, grape processing, and wine quality control is shown in Fig. 1.

## Methodology of the review

The present study was based on a literature search in the databases Web of Science, PubMed, MEDLINE, Scopus, and Google Scholar. The findings of research studies chosen from more than 1000 viewed scientific publications were included/compared (about 85% of the articles were removed due to inconsistency with the issue of wine). The search was based on the phrases "nanomaterials and the analysis of the wine components", "nanoparticles and wine analysis", "biosensors and wine", "quantum dots and glutathione

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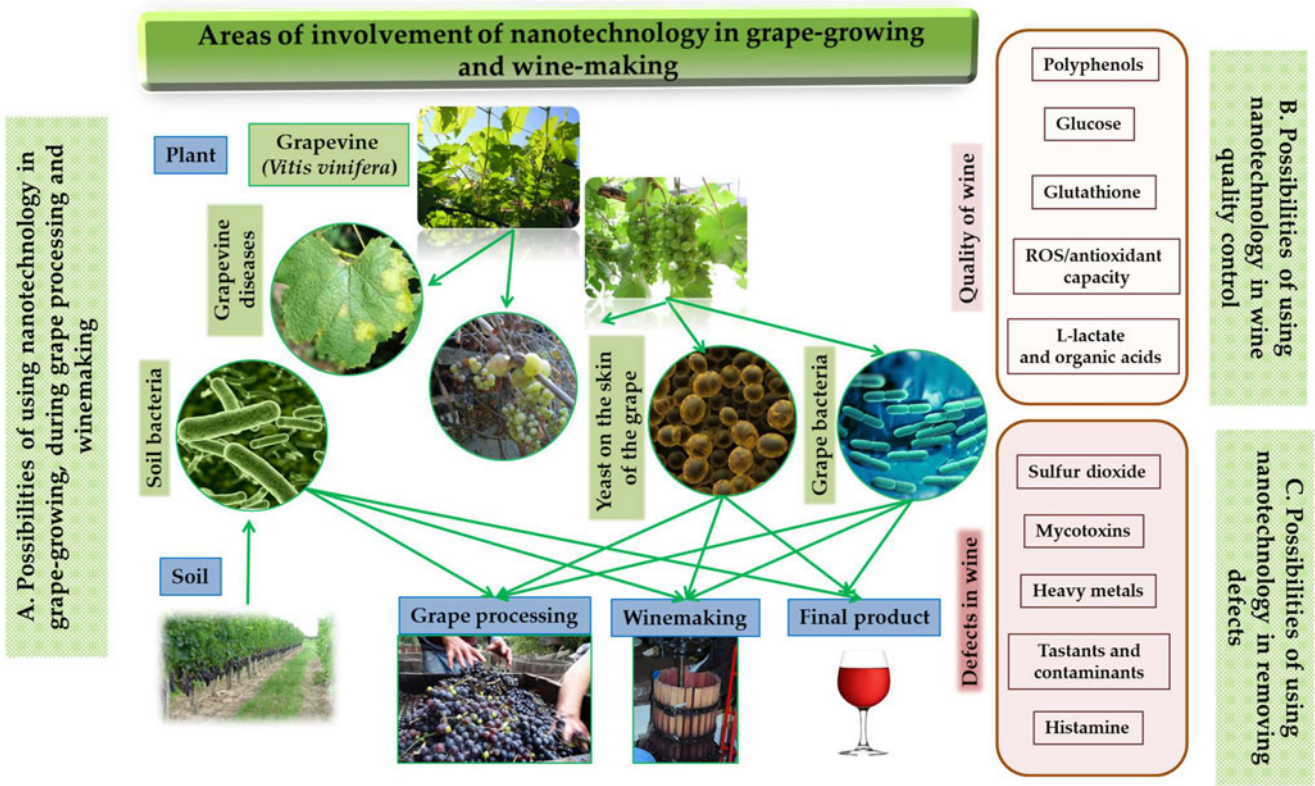


**Figure 1.** Potential nanotechnology applications in grapevine cultivation, grape processing, and wine quality control. Nanotechnology approach can be used not only in analyses of soil microorganisms, grapevine pathogens, but also desirable microorganisms on grapes. Nanomaterial-based analytical systems can also be applied in the production of wine as well as in the quality control of the final product. From the quality control parameters, using the nanotechnology approach it can be analyzed all important compounds in wine, such as polyphenols, lactate, organic acids, glucose, histamine, glutathione, sulfur dioxide, reactive oxygen species (ROS) as well as defects in wine [e.g., Sudan dyes (Yu et al. 2012)]. Nanomaterial-based analyses also allow identifying of tastants and various contaminants such as heavy metals and mycotoxins (Barthelmebs et al. 2011; Lu, Chen, and Hu 2017). Finally, a new method for the rapid separation of wine yeast cells from sparkling wines has recently been developed (Berovic et al. 2014).

analysis", "determination of polyphenols", "lactic acid detection in wine", "magnetic separation of yeast in sparkling wine", "sulfur dioxide in wine", "mycotoxins in wine", "detection of ochratoxin A", "contaminants in wine", "heavy metals and wine", "wine quality and safety", "biosensors for wine quality control", "sulfur dioxide detection in wine", and "biosensors as analytical tools". The present study primarily includes research findings from the years 2002 to 2018.

## Nanomaterials for wine analysis and quality and safety control applications

Nanostructured materials can be used in several analytical devices/systems for qualitative and quantitative determination of wine components, tastants, and preservatives added to wine as well as for the detection of mycotoxins in wine.

### *Nanosensors for analysis of compounds in wine*

Over the past years, unique physical and chemical properties of nanostructured materials have been investigated intensively for electrocatalytic sensing applications (Martin and Mitchell 1998). A biosensor is an analytical device for the detection of a chemical substance that combines a biological component with a physicochemical detector (Khan 2018) and typically consists of a bio-recognition component, biotransducer component, and electronic system which include a signal amplifier, processor, and display (Kaoud Hussein 2015). Fig. 2 illustrates the schematic representation of nanobiosensor, one component of which is a transducer based on nanomaterials. The incorporation of novel nanomaterials especially metallic NPs (Liu et al. 2008; Vidotti et al. 2011; Yáñez-Sedeño et al. 2010), graphene, and carbon nanotubes (CNTs) (Hosnedlova et al. 2019; Yáñez-Sedeño et al. 2010) into electrochemical sensors have substantially increased the stability and the selectivity of electrochemical measurements due to their excellent ability to improve the electron-transfer process (Yáñez-Sedeño et al. 2010). Moreover, the unique electrical properties and high surface-to-volume ratio of the composite nanomaterials such as poly(thionine) can result in a synergic enhancement effect on the electron transfer and enzyme immobilization efficiency compared to the CNT or NP platforms alone (Feng et al. 2007).

Modern sensing technologies use sensors/biosensors to selectively identify the compounds in wine (Barroso et al. 2011). The most frequently analyzed wine components using nanomaterial-based biosensors are presented in Fig. 3. Nanostructured materials increase the surface area of the electrode, which results in enhancing its sensitivity and selectivity of the measuring devices (Barroso et al. 2011). Sensitivity is a key parameter associated with the sensors,

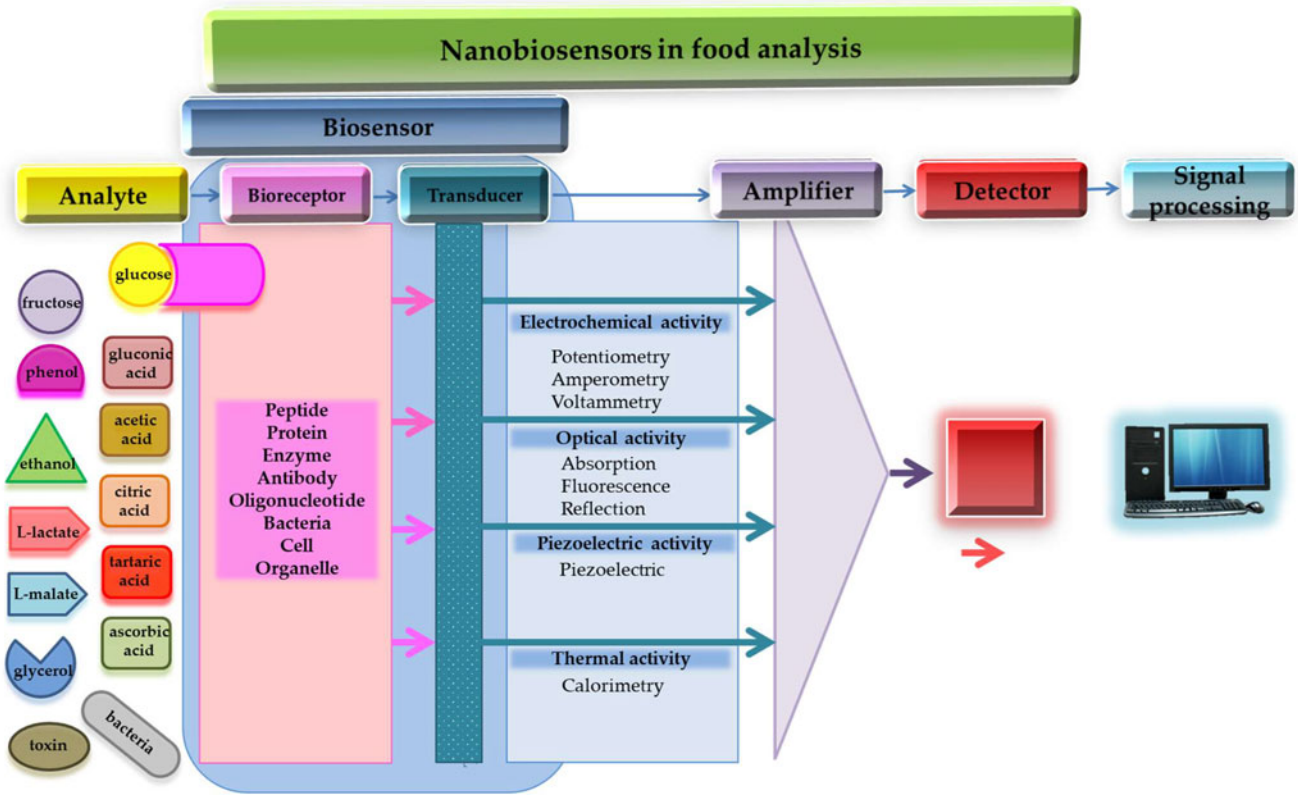


**Figure 2.** Nanobiosensors in food analysis. Analysis using a nanomaterial-based sensor for quantification or detection is composed of components including sample analyte, bioreceptor, transducer with integrated nanomaterials, and detectors. Each sample analyte is unique to the particular bioreceptor – the recognition molecule of the biological origin (e.g., protein, oligonucleotide, microbe, cells, or any subcellular organelle). The biological response is transferred to the detector through a transducer integrated or functionalized with a nanostructured material (e.g., metallic, magnetic nanoparticles, upconversion or molecularly imprinted polymer nanoparticles, quantum dots, carbon-based materials such as graphene oxide, carbon nanotubes, carbon nanofibers, fullerenes, and carbon dots) for enhanced detection via electrochemical, optical and mass detection methods (Srivastava, Dev, and Karmakar 2018).

and it depends on the thickness of the layer deposited onto distinct interdigitated electrodes: the smaller the thickness of the nanostructured film, the higher the sensitivity (Riul Júnior et al. 2003). Riul Júnior et al. (2003) found that, in case of nanostructured thin films of conducting polymers and composite films with a lipid-like material covering interdigitated electrodes, tripling the film thickness (15-layer polypyrrole, Langmuir Blodgett film of 16-mer polyaniline) led to a decrease of almost half of the observed electrical signal (5-layer polypyrrole, Langmuir Blodgett film of 16-mer polyaniline).

For enhancing sensitivity and selectivity, a chemical modification of the electrode surface with some promising nanomaterials such as CNTs, graphene nanosheets or acetylene black NPs can be successfully used. These nanomaterials can be effectively immobilized by simple adsorption. Also, other immobilization strategies can be applied such as electropolymerization of mediator films [e.g., poly(caffeic acid), polyglutamic acid, o-aminophenol], or incorporation of metals (cobalt, copper, nickel) on the electrode composition or formation of self-assembled monolayers (SAMs) (Barroso et al. 2011), or electrodeposition (e.g., gold NPs) (Sanz et al. 2005).

For analysis of components in wine, various NPs have already been used, especially metallic (Ag, ZnO, Au, Pt, $Fe_3O_4$) and molecularly imprinted NPs. Nanoparticles display unique advantages over macroelectrodes when applied for electroanalysis: enhancement of mass transport, catalysis, high effective surface area, and control over electrode microenvironment (Welch and Compton 2006). First of all, molecularly modified metallic NPs are suitable for the preparation of chemical sensors (Haick 2007; Radwan and Azzazy 2009; Saha et al. 2012; Zayats et al. 2005). Among nanomaterials, NPs are the most applied for analysis, followed by carbon nanomaterials and quantum dots (QDs) (Fig. 4).

Immobilization of enzymes onto nanomaterial-modified electrodes allows for the construction of biosensors with very good analytical performance (Putzbach and Ronkainen 2013). Table 1 shows some examples of enzymes used to produce nanostructured enzymatic biosensors applied in wine analysis.

## Application of nanomaterial-based biosensors in wine analysis and their advantages

As in other food sectors, nanosensors have also been used in enology (Karabiberoğlu, Ayan, and Dursun 2013; Sanz et al. 2005; Vasilescu et al. 2016). Scheme of a nanoparticle-based sensor for wine metabolite detection is shown in Fig. 5.

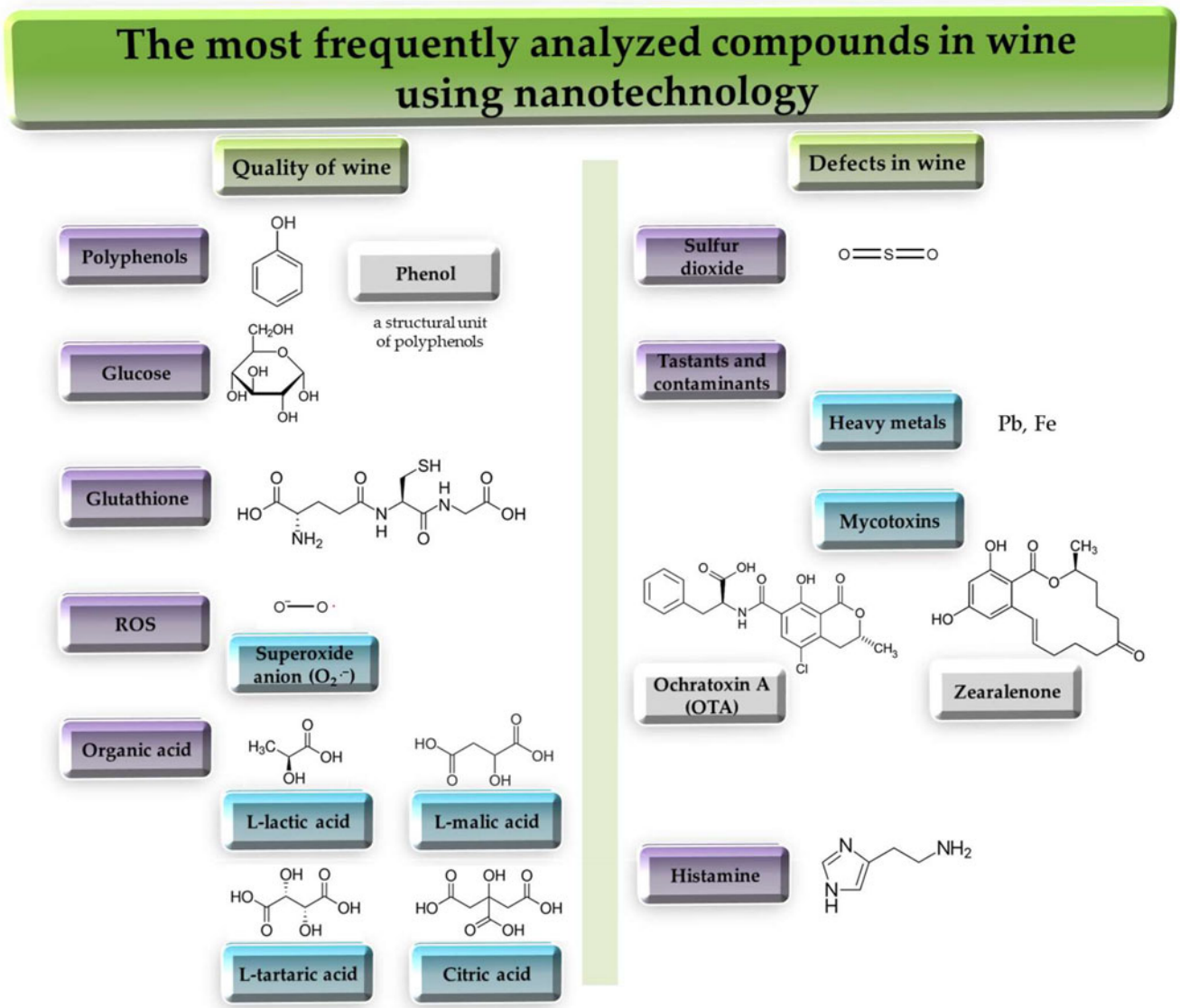


**Figure 3.** The most frequently analyzed compounds in wine using nanotechnology. Both qualitative wine parameters (polyphenols, glucose, glutathione, ROS, organic acids) and wine defects such as sulfur dioxide, heavy metals, mycotoxins, and histamine, can be detected in wine samples. MAA: methacrylic acid.

### *Polyphenol analysis/polyphenol index and determination of polyphenols in wine*

Polyphenols are secondary plant metabolites (Pandey and Rizvi 2009; Quideau et al. 2011; Valdés et al. 2009), which possess important biological activities such as vasodilatatory, anti-inflammatory (Valdés et al. 2009) and prevention of diseases such as cancer, (Bisson et al. 2002; Lopez-Velez, Martinez-Martinez, and Valle-Ribes 2003) cardiovascular diseases (Bisson et al. 2002; Corder et al. 2001; de Gaetano et al. 2003; Dohadwala and Vita 2009; Guilford and Pezzuto 2011; Imhof et al. 2009; Lopez-Velez, Martinez-Martinez, and Valle-Ribes 2003; Pandey and Rizvi 2009; Sano et al. 2007; Valdés et al. 2009), diabetes (Cao et al. 2018; Joosten et al. 2008), osteoporosis, and neurodegenerative diseases (Pandey and Rizvi 2009). Wines contain a whole range of polyphenols including phenolic acids, flavonols (e.g., quercetin and myricetin), flavan-3-ols (e.g., catechin and epicatechin), as well as polymers of the latter (procyanidins and anthocyanins) that are responsible for the color of red wines (Valdés et al. 2009). Red wine is rich in many polyphenols, including resveratrol (Dhir 2018; Pastor et al. 2019) and quercetin, that have been found to evince antioxidant, anti-inflammatory, and neuroprotective properties (Dhir 2018). The first one is considered to be one of the quality standards of red wine. Measuring the trans-resveratrol levels in red wine is necessary for quality control (Liu et al. 2017). Resveratrol can reduce inflammatory mediators. A recent study showed a possible decreasing effect of resveratrol on C-reactive protein (CRP) (Haghighatdoost and Hariri 2019).

The nutritional value of these phenolic components is due to their antioxidant power primarily in red wines (Valdés et al. 2009). Moreover, polyphenols are also responsible for the organoleptic properties of wines (Lorrain et al. 2013). Thus, their detection and quantification are important. The content of polyphenols can vary significantly, for instance, wines from Nuoro (Sardinia) and the Gers area (southwest France) show 2–4-fold increase in biological

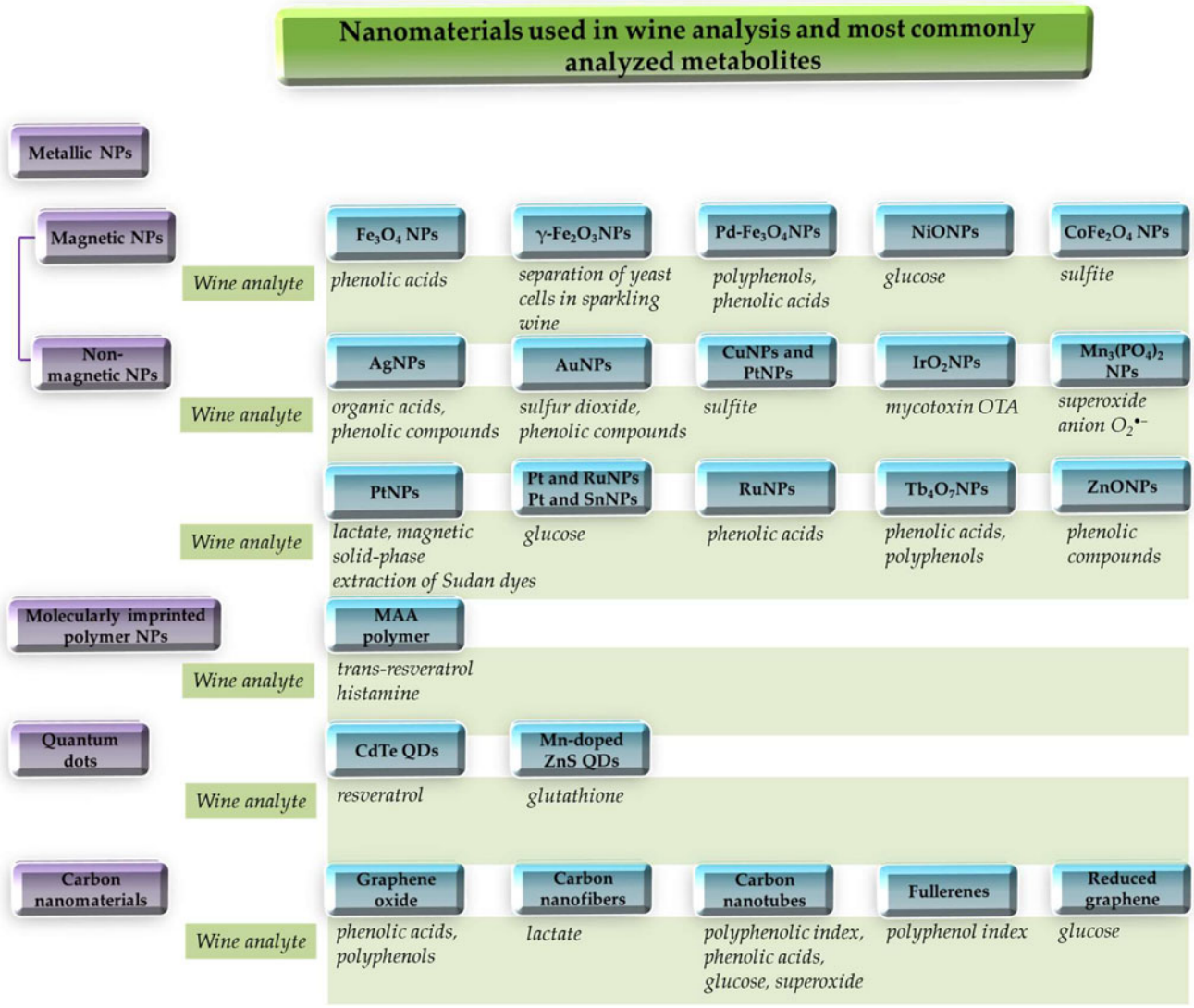


**Figure 4.** Nanomaterials used in wine analysis and most commonly analyzed metabolites. A variety of nanomaterials as part of biosensors can be used to detect metabolites in wine. The most numerous group consists of nanoparticles, either magnetic or non-magnetic, molecularly imprinted polymer NPs, quantum dots and carbon nanomaterials such as graphene, CNTs, carbon nanofibers, and fullerenes.

activity and oligomeric procyanidins (OPCs) content than other wine labels tested from other parts of Italy and France, as well as from Australia, Greece, Spain, South America, and United States (Corder et al. 2006).

The oldest and most commonly used method for determining polyphenols in wine is the photometric method of Folin-Ciocalteu (Magalhães et al. 2006; Nenadis, Lazaridou, and Tsimidou 2007; Sánchez-Rangel et al. 2013). However, this method has the disadvantage of overestimating the content values of these compounds due to the interferences of some non-phenolic reducing compounds (Godoy-Navajas, Aguilar-Caballos, and Gómez-Hens 2015). Therefore, it is necessary to develop more sensitive methods for phenolic compounds determination. One of the possible ways is nanotechnology.

### *Silver nanoparticles and zinc oxide nanoparticles*

Silver nanoparticles (AgNPs) can also be used to determine caffeic acid in red wine. Karabiberoğlu, Ayan, and Dursun (2013) prepared AgNPs decorated poly(thiophene) (PTh) modified glassy carbon electrode (GCE) (Ag/PTh/GCE) for the determination of this compound. The modified electrode exhibited a high electrocatalytic activity towards the oxidation of caffeic acid in red wine samples. The peak current was found linear in the concentration range from 10 nM to 4.83 μM with the limit of detection (LOD) of 5.3 nM ($S/N = 3$). Another application of AgNPs was reported in combination with other types of NPs. A highly sensitive amperometric biosensor by immobilizing laccase covalently onto nanocomposite of AgNPs and zinc oxide nanoparticles (ZnONPs) electrochemically deposited onto gold electrode was used for measurement of total phenolic compounds in wine (Chawla et al. 2012). This technique evinced a good correlation ($r = 0.99$) with the standardly used spectrophotometric method, with the regression equation being $y = 1.0053x - 3.5541$. The constructed biosensor had a long life: it lost 25% of its initial activity after 200 uses over five months.

**Table 1.** Enzymes used for designing nanostructured enzymatic biosensors in wine analysis.

| Method | Detection of analyte | Enzyme | Wine analysis application | Detection limit (LOD) | Reference |
|---|---|---|---|---|---|
| Amperometry | GPE/MWCNTs nanocomposite/ MWCNTs | Glycerol kinase/ creatine kinase/ creatinase/ sarcosine oxidase/ peroxidase | Glycerol in wine | GPE/MWCNTs: 1.96 μM; nanocomposite/MWCNTs: 2.24 μM | (Monošík, Ukropcová, et al. 2012) |
| Amperometry | MWCNTs-SPE SWCNTs-SPE | Laccase – TvL or ThI | Polyphenol index in wine | TvL/MWCNTs-SPE: 0.1 mg · $L^{-1}$; ThL-SWCNTs-SPE: 0.3 mg · $L^{-1}$ | (Di Fusco et al. 2010) |
| Fluorimetry | AuNPs/ indocyanine green | Laccase | Polyphenolic content in red grape juice | Gallic acid 0.04 μM, catechol 0.01 μM, hydroquinone 0.01 μM, hydroxyhydroquinone 0.03 μM, pyrogallol 0.04 μM | (Andreu-Navarro, Fernández-Romero, and Gómez-Hens 2012) |
| Amperometry | Nanocomposite/ AgNPs/ZnONPs | Laccase | Total phenolic content in wine | 0.05 μM | (Chawla et al. 2012 ) |
| Amperometry | GE/AuNPs GE/fullerenols | Laccase | Polyphenols in wine | Gallic acid 6 μM, polyphenol index 1.1 mg ·$L^{-1}$ | (Lanzellotto et al. 2014) |
| Amperometry | CSPE/$MoS_2$/ nanoflakes/GQDs | Laccase | Total polyphenolic content in red wines | Caffeic acid 0.32 μM, chlorogenic acid 0.19 μM, epicatechin 2.04 μM | (Vasilescu et al. 2016) |
| Amperometry | SPE/ferrocene | Laccase Tyrosinase | Phenolic compounds in must and wine | Laccase biosensor: Phenol 620 μM, gallic acid 380 μM, caffeic acid 6 μM, catechin 20 μM, catechol 10 μM; TYR/SPE/ ferrocene: Phenol 10 μM, gallic acid 58 μM, caffeic acid 78 μM, catechin 140 μM; Lac/ TYR/SPE/ferrocene: Phenol: 2 μM, gallic acid: 50 μM, caffeic acid: 24 μM, catechin 40 μM | (Montereali et al. 2010) |
| Amperometry | GE/nanocompositeA/ MWCNT GE/nanocompositeB/ MWCNT | L-lactate oxidase/ peroxidase (LO/PX) | L-lactic acid in wine | GE: 0.96 μM; GE/nanocompositeA/MWCNT/ LO/PX: 1.62 μM; GE/nanocompositeB/MWCNT/ LO/PX: 1.66 μM | (Monošík, Stred'anský, et al. 2012) |
| Amperometry | SPE/PtNPs/GCNFs | L-lactate oxidase | Lactate in wines and ciders | 6.9 μM | (Loaiza et al. 2015) |
| Amperometry | CPE/PBHR/MWCNTs | Peroxidases | Total polyphenolic content in wine | 0.077 mg · $L^{-1}$ and 0.067 mg · $L^{-1}$ for t-resveratrol and caffeic acid, respectively | (Granero 2010) |
| Voltammetry Amperometry | GCE/AuNPs | Tyrosinase | Polyphenols index in red and white wines | Phenol 0.21 μM, catechol 0.15 μM, caffeic acid 0.66 μM, chlorogenic acid 0.62 μM, gallic acid 7 μM, protocatechualdehyde 2 μM | (Sanz et al. 2005) |
| Voltammetry | GCE/MWCNTs | Tyrosinase | Phenolic compounds in red wine | Phenol 100 μM | (Lee et al. 2012) |
| Amperometry | Superparamagnetic nanoparticles/ screen-printed electrodes: Ag electrode, graphite electrode, Ag/ AgCl electrode | Alkaline phosphatase (ALP) | OTA detection in wine | 0.11 ng · $mL^{-1}$ | (Barthelmebs et al. 2011) |
| Voltammetry | SPE/MWCNTs | Laccase (TvL and ThL) immobilized by using polyazetidine prepolymer (PAP) | Polyphenols and catecholamines in real samples | Gallic acid: TvL/MWCNTs/SPE – 0.587–99.92 μM, ThL/MWCNTs/ SPE – 0.587–105.8 μM | (Tortolini et al. 2010) |

AgNPs: silver nanoparticles; ALP: alkaline phosphatase; AuNPs: gold nanoparticles; CPE: carbon paste electrode; CSPE: carbon-based screen-printed electrode; GCE: glassy carbon electrode; GCNFs: graphitized carbon nanofibers; GE: gold electrode; GPE: gold planar electrode; GQDs: graphene quantum dots; Lac: laccase; LO: lactate oxidase; LOD: limit of detection; $MoS_2$: molybdenum disulfide; MWCNTs: multi-walled carbon nanotubes; OTA: ochratoxin A; PAP: polyazetidine prepolymer; PBHR: peroxidases from *Brassica napus* hairy roots; PtNPs: platinum nanoparticles; PX: peroxidase; SPE: screen-printed electrode; SWCNTs: single-walled carbon nanotubes; ThL: *Trametes hirsuta* Laccase biosensor; TvL: *Trametes versicolor* Laccase biosensor; TYR: tyrosinase; ZnONPs: zinc oxide nanoparticles.

### *Gold nanoparticles*

The use of gold nanoparticles (AuNPs) plays an increasingly important role in the preparation of biosensors (Liu, Leech, and Ju 2003). In enology, AuNPs offer their potential in measuring the bioelectrochemical polyphenolic index in red and white wines with the ability to detect a very small volume of sample (270 μL) without the need for pretreatment (Sanz et al. 2005). García-Hernández et al. have successfully improved the sensing properties of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) electrodes towards catechol and hydroquinone sensing using a layer of gold nanoparticles (PEDOT/PSS/AuNPs). The LODs of the thus prepared sensor were for catechol and hydroquinone 2.18 μM and 19.7 μM, respectively. The reported sensor

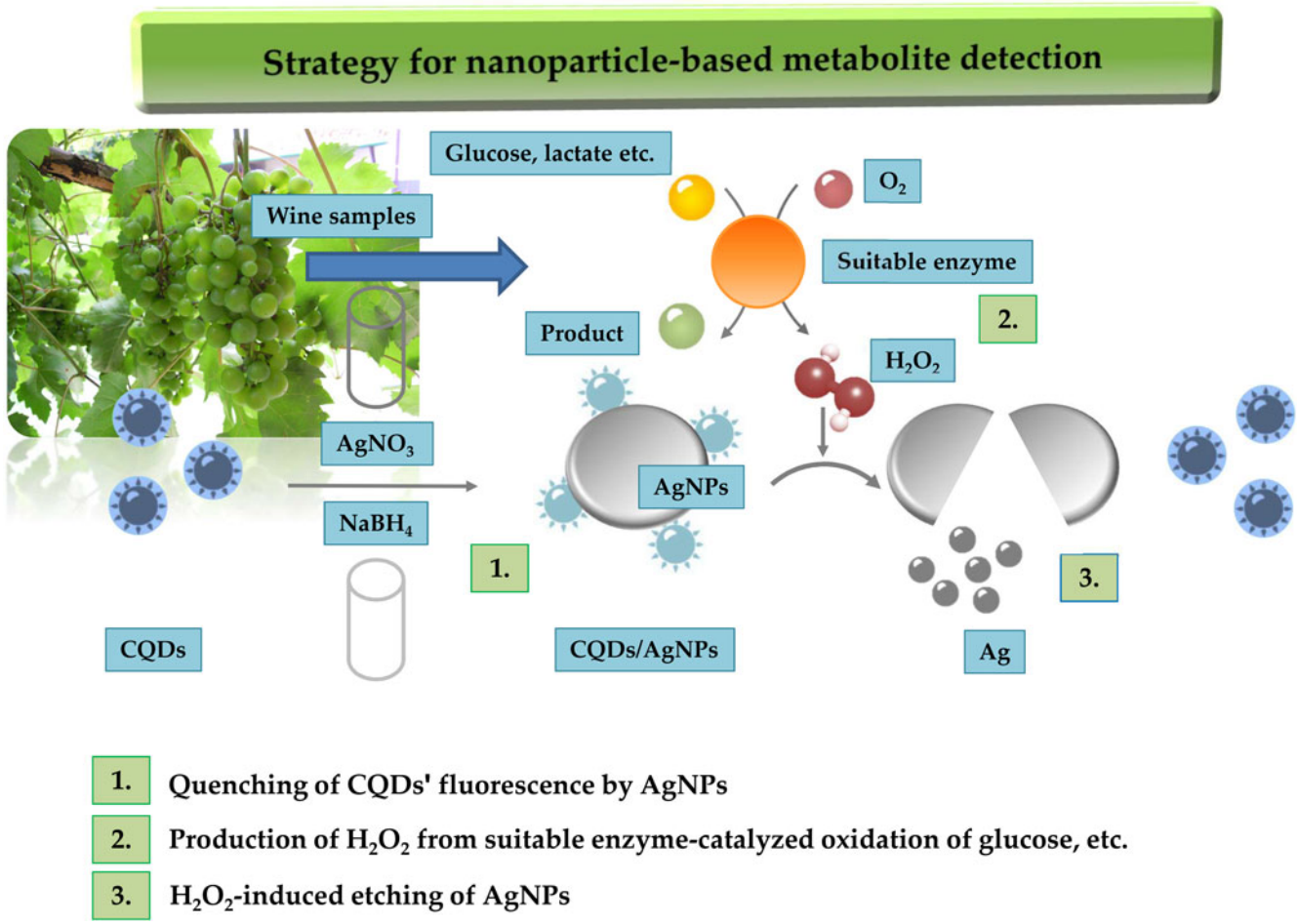


**Figure 5.** A strategy of a possible biosensor for the detection of important molecules (glucose, etc.). Adapted from (Ma et al. 2017). Due to the peroxidase activity of the nanoparticle used and the suitable enzyme, hydrogen peroxide ($H_2O_2$) is generated. For the construction of a biosensor, carbon quantum dots (CQDs)-modified AgNPs are used. Hydrogen peroxide is transferred to AgNPs to produce $Ag^+$ ions resulting in changes in the activity of CQDs. The activity is subsequently recorded by a suitable physicochemical transducer – more details are shown in Fig. 2.

could be applied to analyze the phenolic content of wine (García-Hernández et al. 2016). In another study (García-Hernández et al. 2015), polypyrrole/AuNP (Ppy/AuNP) composites (Ppy/AuNPs films were synthesized by the "trapping method" and were polymerized by chronoamperometry) for sensing catechol were used. The LOD for catechol was 9 µM which is lower than the catechol concentration found in wines thus designed sensor could also be used in wine analysis.

Sanz et al. (2005) developed the tyrosinase biosensor based on AuNPs-modified GCEs for the amperometric detection of phenolic compounds in wine (measuring the bioelectrochemical polyphenolic index in wine). The designed biosensor evinced a good analytical performance and exhibited a fast response to the changes in the concentration of the phenolic compounds including phenol, catechol, caffeic acid, chlorogenic acid, gallic acid, and protocatechualdehyde. A good correlation between the results ($r = 0.990$) was found compared with the spectrophotometric technique.

Chitosan stabilized AuNPs-modified gold electrode can be used for the determination of polyphenol index in wines. This electrochemical sensor was found to be sensitive and selective, and comparing with classical approaches, it offers high sensitivity and rapid response time, for determinations on complex matrices. The LOD of caffeic acid resulted in 25 nM. Moreover, the nanomaterial used enables to avoid the interference of molecules such as ascorbic acid (Curulli et al. 2012).

AuNPs show high selectivity and a very low LOD when determining the polyphenol content of red grape juice using enzyme laccase and the long wavelength fluorimetry system using fluorophor indocyanine green. The method is based on the temporal inhibition caused by polyphenols on the oxidation of the long wavelength fluorophor indocyanine green in the presence of laccase and positively charged AuNPs. The system can be used to measure the following polyphenols: gallic acid, catechol, hydroquinone, hydroxyhydroquinone, and pyrogallol (Andreu-Navarro, Fernández-Romero, and Gómez-Hens 2012).

Gold nanoparticles in combination with an electrochemical biosensor can be used for a fast and almost automated estimation of the fraction of total phenolic compounds and antioxidants in commercial wines (Sánchez-Obrero et al. 2012). Analysis of phenolic acids (caffeic and gallic acids) using Langmuir Blodgett films based on functionalized AuNPs showed enhanced performance due to a combination of electrocatalytic properties of NPs with the high surface-

to-volume ratio of Langmuir Blodgett films. The biosensor achieved very low LODs as low as 1 μM. The excellent catalytic activity of the sensor was also found when using the mixture of phenolic acid and tartaric acid in the range of pH present in wines. Surprisingly, the electrode was able to provide information about concentrations of both compounds with a complete absence of interferences (Medina-Plaza et al. 2015).

### Terbium oxide nanoparticles

Godoy-Navajas, Aguilar-Caballos, and Gómez-Hens (2015) described an automated method for the determination of polyphenols in wine using 8-hydroxypyrene-3-sulphonate trisodium (HPTS) as a new fluorescent laccase substrate and terbium oxide nanoparticles ($Tb_4O_7$NPs) as activators of laccase. Laccase is a phenoloxidase enzyme which catalyzes the oxidation of phenolic compounds to quinones or radicals by reducing the dissolved oxygen to water. The system is based on the temporal inhibition by polyphenols on the decline of the HPTS fluorescence in the presence of laccase and on the activating effect of $Tb_4O_7$NPs. Due to using these NPs, analysis times were shortened and enzyme consumption lowered (Godoy-Navajas, Aguilar-Caballos, and Gómez-Hens 2015).

### Superparamagnetic iron oxide nanoparticles (SPIONs)

Saraji and Ghani (2014) prepared dissolvable layered double hydroxide coated $Fe_3O_4$ magnetic NPs for extraction of phenolic acids such as p-hydroxybenzoic acid, caffeic acid, syringic acid, p-coumaric acid, and ferulic acid which were then separated and quantified using high-performance liquid chromatography-photodiode array detection (HPLC–DAD). The LODs ranged from 0.44 to 1.3 $\mu g \cdot L^{-1}$.

### Palladium impregnated magnetite nanoparticles

Palladium impregnated magnetite NPs (Pd-$Fe_3O_4$NPs) showed a catalytic behavior similar to that of laccase. Pd-$Fe_3O_4$NPs were applied as a reusable catalyst for the fluorometric determination of polyphenols in wines. The proposed technique is based on the decline of the indocyanine green fluorescence, which is ascribed to its oxidation by dissolved oxygen in the presence of the Pd-$Fe_3O_4$NPs, and the inhibition of the fluorescence decrease by polyphenols, which is directly proportional to the polyphenol concentration. The LOD of the method is 0.02 μM, and analytical results are obtained in only several seconds (Godoy-Navajas, Aguilar-Caballos, and Gomez-Hens 2016).

### Fluorescent nanomaterial

Fluorescent carbon nanodots act as sensitive and selective nanoprobes for tannic acid detection in red and white wines. The system can analyze tannic acid without the need of sample pretreatment. Another advantage is the absence of interference from substances commonly present in wines (Ahmed et al. 2015).

### Molybdenum disulfide and graphene quantum dots

Vasilescu et al. (2016) introduced a novel analytical tool applicable for the determination of total polyphenolic content in red wine samples. For its construction, they used a nanocomposite formed from molybdenum disulfide ($MoS_2$) and graphene QDs as electrode modifiers for laccase biosensor. The proposed laccase biosensor has responded efficiently to caffeic acid over a concentration range of 0.38–100 μM, had the LOD of 0.32 μM and a sensitivity of 17.92 $nA \cdot \mu M^{-1}$.

### Cadmium telluride quantum dots

Akshath et al. (2014) proposed a novel optical sensor based on cadmium telluride (CdTe) QDs for ultrasensitive detection of polyphenols. For the construction of the biosensor, laccase was used. This enzyme converts polyphenols to mono- or polyquinones that quench fluorescence of QDs. It was found that proportionate quenching of QDs fluorescence depended on the polyphenol concentration which ranged from 100 μg to 1 $ng \cdot mL^{-1}$. The designed nanosensor allowed detecting individual and total polyphenols at the concentration of 1 $ng \cdot mL^{-1}$. This method evinced much higher sensitivity, specificity as well as selectivity than any other method. Recently, a simple, rapid, and sensitive method for determination of resveratrol in wine samples by using cysteamine (CA) capped CdTe QDs (CdTe-CA QDs) has been introduced (Ramos et al. 2018). It is characterized by a wide linear range from 3.25 to 75 $\mu g \cdot L^{-1}$ with the LOD for resveratrol 0.97 $\mu g \cdot L^{-1}$ and relative standard deviation (RSD) of 3.7% (5.0 $\mu g \cdot L^{-1}$ resveratrol, $n = 10$). This method is inexpensive, suitable for the determination of resveratrol in wine, and comparable with high-performance liquid chromatography (HPLC).

### Carbon nanomaterials

**Carbon nanotubes.** Single-walled and multi-walled carbon nanotubes (SWCNTs, MWCNTs) can be used to determine the polyphenolic index in wine, with the advantage of eliminating interference effects, simple and quick preparation and low cost (Di Fusco et al. 2010). When using MWCNTs to determine the total polyphenol content, high accuracy, short detection time, and a small sample volume are reported (Granero et al. 2010). The use of CNTs with the microbial biosensor (Kim, Kwen, and Choi 2011) and with an electrochemical microbial biosensor, which enables a good electron transfer and high selectivity (Shin, Kwen, and Choi 2011), is considered to be a highly sensitive method for the determination of phenolic compounds in red wines. By using MWCNTs (with amperometric detector), polyphenols in white wine can be detected and quantified. This system represents a highly stable assay of samples with low detection potential (Moreno et al. 2011).

Kim et al. (2009, 2010) mentioned the determination of phenolic compounds in red wine using MWCNTs and a tyrosinase biosensor. This system shows a low LOD and good stability (Lee et al. 2012). Moreno et al. (2011) introduced a method for the detection of four polyphenols

(caffeic, ferulic, gallic acids, and (1)-catechin) and quantification of gallic acid and (1)-catechin in two white wine samples (Cumbre de Gredos and Jaume Serra) by capillary zone electrophoresis with electrochemical detection using MWCNT-modified glassy electrodes in polyethylenimine. The CNT-based electrode was found to be very suitable for its application as an amperometric detector for the capillary zone separation of polyphenolic compounds. Due to its excellent electrochemical properties, the LODs 2.5–3.1 μM (RSD 9–14%) were achieved. The remarkable stability of the electrode signal can be observed even in the presence of potential impurities in the wine. Souza et al. (2011) used CNTs with a modified carbon electrode to determine the antioxidant capacity of red and white wines by direct detection of gallic acid. The advantage of this system is measurement without interfering with glucose and ascorbic acid.

Vilian et al. (2015) proposed a novel catechin sensor based on Pt/$MnO_2$/f-MWCNT modified GCE. This nanosensor exhibited a very low LOD of catechin 0.02 μM and excellent sensitivity (the linear range was 2–950 μM) and is usable for detection of catechin in red wine.

***Graphene oxide.*** The graphene oxide (GO) and 2-aminoethanethiol (2-AET) functionalized GO sheets (AgNPs-AETGO) nanocomposites can be used to design a sensor for the simultaneous determination of quercetin and morin. The linearity ranged, and the LODs of quercetin and morin were 10 nM–5.0 μM and 3.3 nM, respectively (Yola et al. 2014). Introducing graphene film on the electrode surface significantly improves the sensitivity of the sensor response. Liu et al. designed a nanosensor using a graphene-modified GCE which showed high sensitivity due to the μ-μ interaction between the graphene and *trans*-resveratrol, excellent stability, high anti-interference ability, and low LOD of 0.2 μM with a wide linear range of 0.8–32 μM (Liu et al. 2017).

***Graphene oxide and various types of metal nanoparticles.*** For simultaneous detection of quercetin, morin, and rutin in grape wine, ruthenium nanoparticles (RuNPs) and calix[4]amidocrown-5 (C4A5) were synthesized and grafted onto the surface of reduced graphene oxide (RGO) nanocomposite which modified GCE. The simultaneous detection of quercetin, rutin, and morin using RuNPs/C4A5/RGO/GCE biosensor exhibit the LODs of quercetin, morin, and rutin 0.02 nM (Elçin et al. 2016). Cetó et al. (2014) designed a voltammetric sensor in an electronic tongue to evaluate the complete antioxidant profile of red wines. The graphite-epoxy voltammetric sensors were prepared using bare graphite C and adding different modifiers such as cobalt phthalocyanine, conducting polymers (in powder form) such as polypyrrole or polyaniline, copper (CuNPs) and platinum (PtNPs) nanoparticles to the bulk mixture – one component per electrode, plus one unmodified electrode.

### Molecularly imprinted polymers

Wang and Zhang (2007) developed a sensitive, rapid and inexpensive platform based on molecular imprinted polymer (MIP) sensing elements for *trans*-resveratrol detection in wine. The amount of polymer-bound *trans*-resveratrol was quantified using imidazole-catalyzed peroxyoxalate chemiluminescence (CL). A calibration curve was obtained with the LOD of 0.1 μg · $mL^{-1}$. The designed MIP-based CL imaging sensor represents a suitable analytical tool for quick simultaneous detection of *trans*-resveratrol in real samples of both red and white wine. In addition, by using MIP as a recognition element in the CL sensor, the selectivity of the CL technique can be significantly improved.

### Magnetic molecularly imprinted polymers

Another nanomaterial-based resveratrol biosensor utilizes the magnetic molecularly imprinted polymers (MMIPs). Rhapontigenin, which is the analog of resveratrol, was selected as dummy template molecules to avoid the leakage of a trace amount of resveratrol. The MMIPs showed a high adsorption capacity for resveratrol and a fast separation. In real wine samples, the MMIPs exhibited the LOD of 4.42 ng · $mL^{-1}$ (Chen, Xie, and Shi 2013).

### Lipidic nanostructured layers

Medina-Plaza, De Saja, and Rodríguez-Méndez (2014) prepared a nanostructured electrochemical sensor based on phthalocyanines using the Langmuir Blodgett technique. Mixed Langmuir Blodgett films containing arachidic acid (AA) and lutetium bisphthalocyanine ($LuPc_2$) were used for preparing an AA/$LuPc_2$ sensor for determining phenolic antioxidants. The LODs for vanillic acid, catechol, caffeic acid, hydroquinone, gallic acid, and pyrogallol were 133, 4.28, 4.19, 3.34, 3.69, and 26.6 μM, respectively. The system was also able to discriminate grapes of different varieties according to their phenolic content.

## Determination of glucose in wine

Glucose oxidase (GOx), an enzyme catalyst, has been greatly used in the construction of electrochemical biosensors due to its advantages such as high sensitivity and selectivity, response speed, simple instrumentation, and low production cost. On the other hand, enzymatic sensors have low stability, and their application is problematic because of the interference of some electro-oxidizable species (Cui et al. 2006; Dai et al. 2009). Therefore, nonenzymatic sensors based on the direct electrocatalytic oxidation of glucose are currently being developed (Kwon, Kwen, and Choi 2012).

### Nickel nanomaterials

For analyzing glucose, various types of sensors based on nickel oxide NPs (NiONPs) and carbon nanomaterials were prepared for its nonenzymatic detection. For instance, Zhu et al. (2013) prepared a nonenzymatic glucose sensor for measuring glucose in red wines by modifying a GCE with a composite incorporating nickel(II) oxides and reduced graphene was developed. This sensor achieved an LOD of 5 μM. It is sensitive, stable, and reproducible.

Another type of a nonenzymatic nanomaterial-based glucose sensor was fabricated with Cu–Co–Ni nanostructures attached to carbon nanofibers (CNFs) modified GCE with an LOD of 3.05 μM (Liu et al. 2013). Yuan et al. (2013) developed nickel oxide nanoparticles (NiONPs)/GO/glassy carbon (GC) modified electrode by electrodeposition of NiONPs on the GC surface previously modified with GO. The prepared sensor has the LOD of 1 μM. Qiao and Zheng (2012) introduced another type of nonenzymatic glucose sensor based on a GCE electrochemically modified with a nanocomposite prepared from nickel hydroxide and graphene with the lower LOD (0.6 μM).

### Other metal nanomaterials

Other metals used for preparing nanomaterial-based nonenzymatic glucose sensors are Pt, Ru, and Sn. Kwon, Kwen, and Choi (2012) introduced glucose sensors employing MWCNTs with highly dispersed Pt and Ru or Sn NPs fabricated by radiolytic deposition. Comparing with GCE, this proposed sensor based on MWCNTs with bimetallic catalysts exhibited larger currents (mA) than that of a GCE and MWCNT electrode, which can be attributed to the high electrical conductivities of the metallic alloy NPs. The LOD of the glucose sensor was found to be 0.7 mM. Also, the sensor effectively avoided interference from ascorbic and uric acids in a NaOH electrolyte. The sensor is suitable for its application in the detection of glucose in red wine samples.

## Determination of glutathione content in wine

Jin et al. (2016) developed the method for detecting glutathione (GSH) in wine, food, and biological samples, based on the phosphorescent 3-mercaptopropionic acid (MPA) capped Mn-doped ZnS QDs. As the quencher to the phosphorescence of modified QDs, $KMnO_4$ was used. The probable mechanism restoring phosphorescence is as follows: $SO_4^{2-}$ oxidized by $KMnO_4$ on the QDs surface was reduced to $S^{2-}$ with the addition of GSH. The proposed phosphorescent hybrid system provided highly sensitive detection of GSH in aqueous solution with the LOD of 97 nM and a wide linear range of 0.3–280 μM.

## Detection of reactive oxygen species in wine

Nanostructured materials can also be used in reactive oxygen species (ROS) detection. ROS include hydrogen peroxide, superoxide, and hydroxyl radicals, and can mediate chemical reactions that are involved in certain pathogenic processes, resulting in the oxidative stress playing an important role in the development of some diseases, such as cancer and neurodegenerative diseases (Hancock, Desikan, and Neill 2001; Ray, Huang, and Tsuji 2012). Therefore, the detection of ROS concentration in food products is very important. The scavenging capacity of phenolic extracts of a red wine on ROS was confirmed, the most active extract towards superoxide radicals was rich in flavanols and anthocyanins (Roussis, Lambropoulos, and Soulti 2005).

### Carbon nanotubes

For the direct detection of the superoxide, highly sensitive electrochemical biosensors using superoxide dismutase (SOD) by incorporating MWCNTs and polymer poly(3,4-ethylenedioxythiophene) modified GCEs was designed. The biosensor with MWCNTs on top of the polymer had a high sensitivity of about 1115 $\mu A \cdot cm^{-2} \cdot mM^{-1}$ and a low LOD of superoxide anion $O_2^{\bullet -}$ (1 μM) (Braik et al. 2016).

### Gold nanoparticles

Wu, Zhang, and Chen (2014) introduced the superoxide dismutase/L-cysteine/dendritic gold nanostructure/GCE (SOD/Cys/DenAu/GCE) biosensor for superoxide radical ($O_2^{\bullet -}$) detection with a low LOD of 2.1 nM. This biosensor was constructed based on dendritic gold nanostructure (DenAu) attached on GCE, and such a modified electrode was then constructed by assembling L-cysteine onto the DenAu/GC electrode to immobilize large amounts of SOD. Due to the high loading of SOD on the electrode, the biosensor showed a good analytical performance for $O_2^{\bullet -}$ detection, including a low LOD of $O_2^{\bullet -}$ (2.1 nM), good stability, and reproducibility.

### Magnetic polymeric nanotubes

Peng et al. (2017) presented an electrochemical sensor based on magnetic polymeric (polystyrene) nanotubes decorated on their surface with Mn-superoxide dismutase (MnSOD) and $Mn_3(PO_4)_2$NPs for sensitive detection of superoxide anion $O_2^{\bullet -}$. This biosensor evinced an excellent analytical performance, high selectivity, and the linear range from 0.15 to 3.0 μM with an LOD of $O_2^{\bullet -}$ of 0.0136 μM.

## L-lactate and organic acids analysis in wine

During the production of wine, there is alcohol fermentation carried out by yeast and a secondary fermentation conducted by lactic acid bacteria, so-called malolactic fermentation, in which the transformation of L-malic acid into L-lactic acid and $CO_2$ takes place. Besides deacidification, malolactic fermentation affects the flavor, the final taste and the microbiological stability of the wine (Loaiza et al. 2015). Malolactic fermentation is difficult to control and is primarily driven by *Oenococcus oeni*. Uncontrolled secondary fermentation can render the wine unpalatable or even cause spoilage (Bauer and Dicks 2017).

### Platinum nanoparticles

Research on lactate biosensors is already at an advanced stage (Rassaei et al. 2014). Lactate detection in wine using PtNPs supported on graphitized CNFs (in combination with lactate biosensor) significantly simplifies analysis and is a much cheaper alternative to the solid electrodes. Moreover, the method shows long-term stability of enzymatic activity (maintaining at least 90% of the original signal after storing for 3 months at room temperature, or 18 months at −20 °C), sensitivity of measurement ($41{,}302 \pm 546$ $\mu A \cdot M^{-1} \cdot cm^{-2}$,

with a good LOD – 6.9 μM) and good reproducibility (RSD 4.9%). The excellent analytical characteristics make this biosensor a very attractive alternative to conventional methods for lactate determination in wine (Loaiza et al. 2015).

### Gold nanoparticles

Nanomaterial-based biosensors are also developed to detect other organic acids typically occurring in wine. A chemically modified electrode consisting of Langmuir Blodgett films of *n*-dodecanethiol functionalized AuNPs was investigated as a voltammetric sensor of main organic acids present in grapes and wine (tartaric, malic, lactic, and citric acids). AuNPs increased the sensitivity toward organic acids significantly. A very low LOD (1 μM) was achieved. The designed sensor was able to provide information without any interference (Medina-Plaza et al. 2015). Molinero-Abad et al. (2014) reported malate quinone oxidoreductase biosensor based on tetrathiafulvalene and AuNPs modified screen-printed carbon electrodes for the detection of malic acid in wine. This modification improved the sensitivity for the analysis of this compound and the prepared sensor showed a capability of detection for malic acid of 2.0 μM.

### Carbon nanotubes

MWCNTs (with an amperometric biosensor) can also be used to detect L-lactic acid in wines – the device allows to determine the low concentration of lactic acid (Monošík, Stred'anský, et al. 2012) and is also useful for the determination of glycerol in wine (Monošík, Ukropcová, et al. 2012) to ensure monitoring of malolactic fermentation and glycerol monitoring during wine production process (Monošík, Stred'anský, et al. 2012; Monošík, Ukropcová, et al. 2012).

## Detection of preservatives and undesirable compounds in wine

### Determination of sulfur dioxide in wine

Sulfite, a commonly used preservative of wine, prevents oxidation, inhibits bacterial growth, and controls enzymatic and nonenzymatic reactions (Gunnison, Jacobsen, and Schwartz 1987). On this basis, the U.S. Food and Drug Administration (FDA) has required labeling of products containing more than 10 $\mu g \cdot mL^{-1}$ sulfite in food or beverages since 1986 (Lawrence and Chadha 1988). According to Commission Regulation (EC) No 606/2009 of 10 July 2009, the total sulfur dioxide ($SO_2$) content of wine, with the exception of sparkling and liqueur wines, at the moment of putting into circulation for direct human consumption, exceed the following values: (a) 150 mg per liter for red wine; (b) 200 mg per liter for white and rosé wine. In this respect, the determination of sulfite compounds in wine is particularly important.

***Superparamagnetic iron oxide nanoparticles (SPIONs).*** Magnetic ($Fe_3O_4$) NPs (with an electrochemical biosensor) can be used to measure sulfate levels in red and white wine. The system based on carboxylated gold-coated magnetic NPs electrodeposited onto the surface of a gold electrode is characterized by a low LOD (0.15 μM), low reaction time (2 s) and measurement without interfering with ascorbate, cysteine, fructose, and ethanol (Rawal, Chawla, and Pundir 2012). Zhang et al. (2013) reported $CoFe_2O_4$ nanoparticles as oxidase mimic-mediated chemiluminescence of aqueous luminol for the determination of trace amount of sulfite in white wines. The presented system could respond down to 20 nM sulfite. The results obtained by the proposed method were in good agreement with those given by the standard titration method.

***Gold nanoparticles.*** AuNPs (with electrochemical sensor) are also suitable for highly sensitive and ultrafast determination of $SO_2$ preservative in white wines without interference with polyphenols. The advantage of this sensor is the ability to analyze a small sample volume and low cost (Schneider et al. 2014).

### Mycotoxins detection

Mycotoxins are toxic secondary metabolites produced by filamentous fungi and can contaminate food commodities, including grapes and wine (Serra, Braga, and Venâncio 2005). High amounts of mycotoxins in the diet can cause adverse effects on human health, which can manifest as acute or chronic. Side effects can affect many body organs and systems such as the liver, kidney, nervous system, endocrine system, and immune system (Malhotra et al. 2014). The conventional methods of analysis of mycotoxins normally require sophisticated instrumentation, e.g., liquid chromatography (LC) with fluorescence or mass detectors, combined with extraction procedures for sample preparation. Thus, new analysis tools are necessary to attain more sensitive, specific, rapid, and reliable information about the desired toxin (Malhotra et al. 2014). In grapes destined for wine production, the most frequent genera of fungi were detected as follows: *Cladosporium, Alternaria, Botrytis, Penicillium*, and *Aspergillus* (Serra, Braga, and Venâncio 2005). In the study of Serra, Braga, and Venâncio (2005) focused on the isolation of mycotoxigenic species from grapes, the most frequently occurring species were *Aspergillus niger aggregate*, *Aspergillus carbonarius*, *Fusarium* spp., and *Trichothecium roseum*. The first two strains belong to the most important producers of mycotoxin ochratoxin A (OTA) (Serra, Braga, and Venâncio 2005), which is considered one of the most feared mycotoxins in wine. Besides OTA, other plentiful mycotoxins considered most relevant for human health by the Council for Agricultural Science and Technology (CAST) are aflatoxins, trichothecenes, fumonisins, zearalenone, and ergot alkaloids (Council for Agricultural Science and Technology 2003). OTA is a known secondary fungal metabolite which contaminates a variety of food commodities and exhibits many toxicological adverse effects such as nephrotoxic, hepatotoxic, neurotoxic, teratogenic, and immunotoxic (Hayat et al. 2013). OTA was found to be potentially carcinogenic to humans and has also been shown to be weakly mutagenic, possibly by induction of oxidative DNA damage (Palma et al. 2007). For mycotoxin

determination, immunological techniques based on specific monoclonal and polyclonal antibodies produced against several toxins are commercially available. These methods are suitable for rapid qualitative screenings. However, they cannot determinate an accurate quantity of the toxin. The analytical methods with good accuracy, precision, sensitivity, and reproducibility that are traditionally used for the detection of mycotoxins are primarily chromatographic-based techniques, e.g., HPLC (Pohland and Trucksess 2001) or gas chromatography (GC) (Lehotay and Hajšlová 2002; Sforza, Dall'Asta, and Marchelli 2006). These methods, however, require demanding sample preparation, time-consuming and highly trained personnel. Also, they often use a large number of hazardous reagents for analysis. Due to the potential carcinogenic, teratogenic, and mutagenic effects of mycotoxins, and their wide existence in food products, rapid, high-throughput and portable methods for sensitive detection are needed (Guo et al. 2015).

For the detection of OTA in wine, various nanotechnology-based methods have also been developed and are presented below.

***Silver nanoparticles and ruthenium nanoparticles.*** Jiang et al. (2017) have developed AgNP-based fluorescence-quenching lateral flow immunoassay with a competitive format for highly sensitive detection of OTA (LOD of 0.06 $\mu g \cdot L^{-1}$) in grape juice and wine samples. The AgNPs, due to their ability to block exciting light transferring to the ruthenium nanoparticle (RuNP) molecules, served as the fluorescence quenchers of RuNPs. The dynamic linear range was from 0.08 to 5.0 $\mu g \cdot L^{-1}$. The proposed method for quantitative detection of OTA in wine is simple, rapid, sensitive, and accurate.

***Magnetic nanoparticles.*** Amine-functionalized magnetic nanoparticles (MNPs) can serve for the rapid and sensitive determination of mycotoxin OTA in red grapes (Fernández-Baldo et al. 2010). The electrochemical determination of OTA based on a DNA aptamer sensor using supermagnetic NPs is highly sensitive, cost-effective, and a rapid method (Barthelmebs et al. 2011). With high sensitivity and specificity, OTA can also be determined using iron oxide carboxyl-modified magnetic NPs (with an electrochemical impedance spectroscopic immunosensor). The advantages of this system include speed and economic efficiency (Zamfir et al. 2011). Fernandez-Baldo et al. (2010) introduced an electrochemical method based on modified MNPs and square wave voltammetry (SWV) which had exhibited a rapid and sensitive detection of OTA in wine grapes with the LOD of 0.02 $g \cdot kg^{-1}$. Barthelmebs et al. (2011) introduced an electrochemical DNA aptamer-based biosensor for OTA detection, using superparamagnetic NPs. The principle is based on the competition of free OTA with labeled alkaline phosphatase(ALP)–OTA for the binding to the DNA aptamer immobilized on magnetic beads. The electrochemical detection is thus performed through an appropriate substrate for the enzyme ALP, by differential pulse voltammetry (DPV). The proposed aptasensor enabled the LOD of 0.11 $ng \cdot mL^{-1}$ (Barthelmebs et al. 2011).

***Iridium oxide nanoparticles.*** Rivas et al. (2015) designed a new nanostructured platform based on iridium oxide nanoparticles ($IrO_2$NPs) for OTA detection in white wine. An aptasensor was based on a screen-printed carbon electrode (SPCE) modified with polythionine (PTH) and $IrO_2$NPs. The system achieved a very low LOD for OTA which had been reported for its label-free impedimetric detection (14 pM; 5.65 $ng \cdot kg^{-1}$) and was highly specific against a toxin zearalenone that could interfere in the detection of OTA in white wine samples.

***Other nanomaterials.*** Recently, Lu, Chen, and Hu (2017) developed an aptasensor based on semiconductor QDs (acts as a donor) and molybdenum disulfide ($MoS_2$) nanosheets (as quenchers) showing a good performance in detecting OTA in red wine samples with the LOD of 1.0 $ng \cdot mL^{-1}$.

### Heavy metals detection

The Organization International de la Vigne et du Vin (OIV) fixed an uppermost level for some heavy metals in wine. In connection with this, it has become necessary to determine the very low concentrations of heavy metals that can occur in wine in trace or ultra-trace amounts (Voica, Dehelean, and Pamula 2009). Therefore, their quantification and strict analytical control of metal concentration are required during the whole process of wine production (Tariba 2011). The further application of QDs in wine analysis represents their use for the detection of toxic elements. However, few scientific papers are focusing on the nanotechnology-based detection of heavy metals in wine samples; the studies are more generally concerned with their determination in liquid samples. For example, Hai, Yang, and Li (2013) constructed an electrochemiluminescence sensor using QDs based on a G-quadruplex aptamer for $Pb^{2+}$ detection. The designed biosensor evinced good selectivity, stability, and reproducibility, and the LOD was found to be 0.0108 nM.

Nanostructured thin films of conducting polymers [Langmuir Blodgett films of 16-mer polyaniline (16-mer), polypyrrole (PPy), stearic acid (SA)] and composite films of 16-mer/SA and PPy/SA deposited onto gold interdigitated electrodes can also be used for the detection of trace amounts of inorganic contaminants in liquids. The sensor can detect and differentiate the level of toxic ions of 0.05 mg $\cdot L^{-1}$ such as $Pb^{2+}$ and $Cr^{4+}$. The electronic tongue allowed also distinguish brands of three red wines with regard to vintage and chemicals added without complex laboratory analysis (Riul Júnior et al. 2003).

Camara-Martos et al. (2016) introduced a fast, disposable, and label-free biosensor for quantification of $Fe^{3+}$ in food liquid samples such as wine. The biosensor is based on a field effect transistor where a network of SWCNTs acts as the conductor channel. As immunoreaction, an antibody – transferrin with two specific high-affinity $Fe^{3+}$ binding sites was directly adsorbed to SWCNTs. The biosensor prepared

showed a very low limit of quantification (below 0.05 ng · $mL^{-1}$) compared with other analytical techniques.

### Detection of some defects in wine

In the last decade, so-called electronic tongues were developed. Gutiérrez et al. (2010) introduced a voltammetric electronic tongue fabricated from epoxy-graphite electrodes for the qualitative analysis of wine. The electronic tongue was formed by five voltammetric electrodes, four of them being modified with CuNPs and PtNPs on one side, and polyaniline and polypyrrole powder on the other side. This analytical tool is usable to the detection of some defects in wine production such as its vinegary taste in open-air contact or the excessive amount of sulfite preservative (Gutiérrez et al. 2010). Using nanocomposites, it can also be extracted Sudan dyes from wines. Yu et al. (2012) synthesized polystyrene-coated magnetic NPs which used as an excellent adsorbent for magnetic solid-phase extraction of four Sudan dyes (I, II III, and IV) in red wines, juices, and mature vinegar which were then detected by ultrafast liquid chromatography-ultraviolet spectrometry (Yu et al. 2012).

### Detection of tastants and suppression of sourness by the sweetness

The development of artificial sensors for the detection, quantification, and evaluation of tastants in liquid systems is very important for the food and beverage industry (Riul Júnior et al. 2003). In the last two decades, a great effort has been devoted to the development of "electronic tongues" mimicking the biological system (Blanco et al. 2015; Buratti et al. 2015; Costa et al. 2015; Daikuzono et al. 2015; Di Natale et al. 2000; Ha et al. 2015; Ivarsson, Holmin, et al. 2001; Ivarsson, Kikkawa, et al. 2001; Krantz-Rülcker et al. 2001; Nery and Kubota, 2016; Phat, Moon, and Lee 2016; Riul et al. 2002; Sakai, Iiyama, and Toko 2000; Takagi et al. 2001; Toko, 2000; Vlasov et al. 2000; Winquist et al. 2000). Pure and composite nanostructured films of conducting polymers (16-mer polyaniline, polypyrrole, and stearic acid) deposited onto gold interdigitated electrodes can be used for detection of trace amounts of tastants in liquids, and detection of the suppression of sourness by sweetness displaying similarities with the biological system. This device acts as an artificial taste sensor (electronic tongue), which is more accurate than the classic sensory test, with a good distinction of tastants at 5 mM which is below the human threshold for saltiness and sweetness. It can also be used for testing different wines with regard to vintage and adulteration. For example, the sensor was able to separate Cabernet Sauvignon wines easily from one in which sugar and conservatives were added to feature some taste characteristics (Riul Júnior et al. 2003).

### Determination of histamine in wine

Molecularly imprinted NPs were used to develop a promising tool for direct quantification of histamine in wine. Basozabal et al. (2014) prepared a novel potentiometric sensor based on molecularly imprinted NPs produced via the solid-phase imprinting method. The constructed sensor was able to selectively quantify histamine in the presence of other biogenic amines in real wine matrices. The LOD achieved the value of 1.12 µM, with a linear range between 1 µM and 10 mM and a short response time below 20 s.

### Effect of nanoparticles on microorganisms in wine/controlling undesirable microorganisms in wine/control of malolactic fermentation

Recently, the link between the genetically differentiated microbial populations of the grapevine/wine grapes and influencing the wine phenotype has been extensively discussed (Bokulich et al. 2014; Gilbert, van der Lelie, and Zarraonaindia 2014; Knight et al. 2015; Mezzasalma et al. 2017). Regional microbial signatures positively correlate with differential wine phenotypes, which is evidence for a microbial aspect to *terroir* (Knight et al. 2015). The unique microbial flora ensures regional wine fermentations, and the existence of this "microbial terroir" is a determining factor in regional variation among wine grapes (Bokulich et al. 2014). These findings suggest the importance of microbial populations for the regional identity of wine (Knight et al. 2015).

Nanotechnology is also utilized in controlling microbial processes in winemaking. For controlling the growth of lactic acid bacteria and acetic acid bacteria in wines, GSH-stabilized AgNPs can be used. These modified NPs possess an extraordinarily efficient inhibitory potential against Gram-negative and Gram-positive bacteria, such as *Escherichia coli* and *Staphylococcus aureus*, and different wine lactic acid bacteria (*Oenococcus oeni, Lactobacillus casei, Lactobacillus plantarum,* and *Pediococcus pentosaceus*) and acetic acid bacteria (*Acetobacter aceti* and *Gluconobacter oxydans*) (García-Ruiz et al. 2015).

Dušak et al. (2016) developed a novel method for magnetic separation of the magnetized lactic acid bacteria (LAB) *Oenococcus oeni* at a desired stage of the malolactic fermentation in wine. Superparamagnetic amino-functionalized silica-coated maghemite NPs were bonded to the bacterial surface in the suspension. Subsequently the "magneto-responsive" bacteria (MRB) in the fermentation process were applied and then their magnetic separation from the wine using high-gradient magnetic separation (HGMS) followed which resulted in a stop of the fermentation process. Manzano et al. (2016) designed localized surface plasmon resonance (LSPR) genosensor for the rapid and sensitive detection of the spoiler wine yeast *Brettanomyces bruxellensis*. For nanosensor construction, they used a nanostructured gold surface for the immobilization of a 5′ end thiol modified DNA probe. Incident light interacting with noble-metal nanoparticles with smaller sizes than the wavelength of the incident light induces LSPR. Substrates based on annealed AuNPs were modified with oligonucleotides. LSPR technique showed high specificity for *B. bruxellensis* detection (0.1 ng · $mL^{-1}$).

### Separation of yeast cells in sparkling wine

Berovic et al. (2014) developed a novel method for the rapid magnetic separation of wine yeast cells from sparkling wine.

The method is based on the ability of the magnetized yeast to be magnetically separated from the suspension. They prepared the magnetically responsive yeast cells by the adsorption of the superparamagnetic NPs (iron-oxide maghemite – $\gamma$-$Fe_2O_3$) coated with a thin layer of silica and grafted with (aminoethylamino)propylmethyldimethoxysilane (APMS) onto their surfaces. The separation of the magnetized waste biomass in the bottleneck using relatively weak magnetic-field gradient is completed in 15 min. On the contrary, the traditional method requires about 60 days of manual rotation and elevation of each bottle. The magnetic NPs remained fixed at the microbial cell surfaces, even after fermentation, and besides increasing the rate of microbial kinetics, they did not influence the cellular metabolism of the yeast (Berovic et al. 2014). Iron-oxide NPs are considered to be nontoxic and were even approved by the American Food and Drug Administration (FDA) for in vivo medical applications (Thanh 2012). The measured value of $Fe^{3+}$ ($8.30 \pm 0.16\,mg \cdot L^{-1}$) in the sparkling wine prepared using iron-oxide NPs did not proceed the permissible limit for iron concentration in white wine (Berovic et al. 2014).

### *Discrimination of wines using electronic tongues*

Recently, an impedimetric electronic tongue based on nanomaterials to discriminate red wines with similar characteristics (same region, vintage and aging method) has been developed. The multisensor system was constructed using PEDOT-PSS layered nanocomposites [one PEDOT:PSS sensor and two nanocomposites formed by layers of PEDOT:PSS and gold nanoparticles (PEDOT:PSS/AuNP) or layers of PEDOT:PSS and lutetium bisphthalocyanine (PEDOT:PSS/$LuPc_2$)]. Due to the application of nanolayers of $LuPc_2$ and AuNPs, sensors exhibited remarkable sensing properties. This improved electronic tongue was able to discriminate three wines from the variety Tempranillo, one wine of the variety Tinta de Toro (a clone of Tempranillo) and one wine elaborated with a coupage of 90% Tempranillo and 10% Garnacha variety. The discrimination was based on the analysis of various parameters such as folin, total polyphenol index, total acidity, $SO_2$, reducing sugar, glucose, and fructose, alcoholic degree, and pH (Garcia-Hernandez et al. 2018).

Rodriguez-Mendez et al. developed an electronic tongue formed by nanostructured voltammetric biosensors based on biomimetic Langmuir Blodgett films containing phthalocyanines combined with tyrosinase, laccase or glucose oxidase in an amphiphilic matrix for analyzing wines and grapes. These nanosensors had exceptional properties due to the high number of active sites. Phthalocyanines act as electron mediators and improve the performance of the sensor. The selectivity of the electronic tongue and its capability of discrimination were markedly enhanced when the biosensor contained glucose oxidase or tyrosinase. The improvement in the performance has been evaluated by testing solutions of catechol, glucose, and musts prepared from grapes of different wine varieties: Tempranillo, Prieto Picudo, Mencía, Cabernet, and Garnacha (Rodriguez-Mendez et al. 2014).

## Conclusions

Nanotechnology is increasingly penetrating the food sector. In enology, it is mainly used to improve the properties of analytical equipment for qualitative and quantitative determination of compounds in wine. The potential for its use is offered throughout the entire production process – from growing grapes through wine production to bottling. For sparkling wines, a new rapid method of separating yeast biomass by magnetic nanoparticles has already been designed. In the future, the improvement of the quality characteristics of the wine is expected in the implementation of the nanotechnological processes. However, from a safety point of view, further research on the relationship of nanostructured materials to human health is needed.

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The authors declare no conflict of interest.

## Author contributions

All authors have contributed to the content of this paper.

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