Chapter

Electrochemical Applications for the Antioxidant Sensing in Food Samples Such as Citrus and Its Derivatives, Soft Drinks, Supplementary Food and Nutrients

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Abstract

Although there are many definitions of antioxidants, the most general description; antioxidants are carried a phenolic function in their structure and prevent the formation of free radicals or intercept from damage to the cell by scavenging existing radicals. Moreover, they are one of the most effective substances that contain essential nutrients for healthy individuals. The importance of these antioxidants, which have an incredible effect on the body and increase the body's resistance, is increasing day by day for healthy individuals. Numerous studies have been carried out for antioxidants with excellent properties and however new, reliable, selective, sensitive and green analytical methods are sought for their determination at trace levels in food samples. Along with the latest developments, electrochemical methods are of great interest in the world of science because they are fast, reliable, sensitive and environmentally friendly. Electrochemical methods have been frequently applied to analyze antioxidant capacity in many nutrients samples found in different forms such as solid, liquid without any pretreatment applications in the last decade. Furthermore, these methods are preferred because of the short analysis time, the ability to lower detection limits, reduction in a solvent, high sensitivity, portability, low sample consumption, wide working range, and more economical than existing other traditional analytical methods. The antioxidant sensing applications by modern electrochemical methods such as cyclic, square wave, differential pulse, and combined with stripping voltammetric techniques were used to deduce antioxidant capacity (AC) in critical nutrients. Moreover, this chapter includes a description of the classification of electrochemical methods according to the working electrode type, dynamic working range, limit of determination (LOD), limit of quantification (LOQ), sample type, and using standard analyte and so forth for each voltammetric methods. While many articles applied for the determination of antioxidant sensing by electrochemistry have gained momentum in the last two decades, we focused on the studies conducted over the last 4 years in this chapter.

Keywords: antioxidant determination, electrochemistry, voltammetric methods, potentiometry, amperometry

1. Introduction

Free radicals occur when an atom or molecule contains one or more unpaired electrons in its outermost orbitals [1]. Basically, three main factors play a role in the formation of free radicals. i) The atoms or molecules can become radical as a result of the fragmentation of covalently bonded molecules exposed to high-energy electromagnetic waves or high temperatures. ii) A molecule that does not have a radical feature experience an electron loss and radicals are formed by leaving unpaired electrons in its outer orbital. iii) A radical is formed when a molecule that does not have a radical property receives an electron from outside and has an unpaired electron in its outer orbital [1, 2]. These unshared electrons as known radicals are highly unstable, transforming them into high-energy and very efficient chemical species. The most active free radicals in biological systems are those based on oxygen and are commonly referred to as reactive oxygen species (ROS) with pathological [3]. This family group includes superoxide radical ($O_2^{\cdot}$), singlet oxygen, nitroxide (NO), hydroxyl radical ($OH^{\cdot}$), and hydrogen peroxide (H_2O_2) which is not itself radical but causes the formation of radical [1]. Besides, we can classify the causes of free radicals in two groups as endogenous or exogenous [1, 2]. Cigarettes, air pollution, alcohol, radiation, heavy organic solvents and pesticides are among exogenous sources, while enzymes, proteins, oxidative stressors, and heavy metals are endogenous sources [1, 4].

Free radicals cause the greatest damage to human health on basic cellular components such as lipids, proteins and nucleic acids [1, 5]. Therefore, these radicals lead to immune deficiency, hypertension and even important diseases such as cancer, neurodegenerative diseases, heart disease, and atherosclerosis [1, 2]. Also, studies are revealing that radicals disturb the homeostatic balance [6]. To scavenge these drawbacks effects of radicals, which are extremely important for human health, the human body needs antioxidants obtained from the body or nutrition to fulfill biological activities such as survival and healthy life. Antioxidants can be defined as molecules that usually contain phenolic functional groups in their structure and prevent the formation of free radicals that damage the cell or by scavenging existing radicals [3]. The functional task of antioxidants is that they act as shields in the body and neutralize them by donating their electrons with the s-free radicals. Thus, radicals found in a rather unstable structure do not become a threat to human health by transforming into a more stable structure reacted with antioxidants. Moreover, many different equivalent antioxidant expressions are used in antioxidant quantification in food samples. The leading ones are the expressions of "total antioxidant capacity (TAC)", "antioxidant activity (AA)", and "antioxidant capacity (AC)". The total amount of antioxidants is expressed by measurement units such as equivalent trolox, rutin, ascorbic acid, and quercetin, etc.

Antioxidants are mainly obtained via natural and synthetic [7]. The first of these, natural antioxidants, are molecules synthesized by the organism or obtained from food sources. Natural antioxidants produced by the organism are the most important source for human health. Many factors affect the production process of this natural antioxidant. The most important of these is the age of the person. As a person gets older, the amount of natural antioxidants produced by his organism decreases day by day. For this reason, there is a greater need for the natural antioxidants found in foods for older people. The importance of healthy food sources, especially organic-based foods, is increasing day by day. Also, such nutrients should be accessible to all segments of society.

Important dietary flavonoid sources are fruits especially citrus fruits such as oranges, apples, grapes, mandarins, berries lemons, limes and their derived products as well as juices [8]. In general, citrus fruits contain pectin, sugar, carotenoid

pigments, vitamins (A, B1, and C), and; organic acids such as ascorbic acid and citric acid, minerals and a number of active phytochemicals such as flavonoids and coumarins, as naringenin, naringin, hesperidin, neohesperidin, hesperetin, rutin, narirutin and tangeretin [9]. For example; polyphenol antioxidants such as flavanols (epicatechin, catechin), phenolic acids (caffeic acid and gallic acid), anthocyanins (e.g., malvidin-3-glucoside), oligomeric and polymeric proanthocyanidins, flavonols (myricetin, quercetin, and their glycosides), and many others polyphenols exist in wine, especially in red wine [10]. Flavonoids have an important role in scavenging reactive oxygen species, which can counteract lipid oxidation, decrease peroxide formation in vivo, and improve activity of the body's antioxidant enzyme. Citrus flavonoids such as naringin, naringenin, and hesperidin have antioxidant activity [11]. Naringenin is a flavonoid, particularly a flavanone, found in citrus fruits especially oranges and grape fruits and in vegetable's such as tomatoes and their preparations. The pharmacological and biological properties of phytoestrogen naringenin and its derivatives include, anticancer, anti-inflammatory, antiulcer, antifibrotic, diastolic, antioxidant and skin protective effects [8]. Also, citrus species are a rich source of flavanone glycosides such as hesperidin and narirutin, which have anticancer, antioxidant, antiobesity and anti-inflammatory activities [12].

Secondly, the antioxidant group is synthetic, that is a molecule that is obtained as a result of chemical reactions and is generally used as food preservatives [13]. Synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and tertiary butylhydroxyquinone (TBHQ) also extend the shelf life of foods [14]. However, natural antioxidants that can be taken from foods are less risky in terms of human health since synthetic antioxidants can have toxicity even if they are very little, they require high costs and have less capacity than natural antioxidants. Due to this reason, the investigations of foods types that can contain high levels of antioxidants in different types of endemic, organic and traditional food samples have been remarkably increased recently.

For antioxidant content and amount analyzes, oxygen radical absorbance capacity (ORAC) and radical-arrest antioxidant parameter (TRAP), ferric thiocyanate (FTC), Trolox equivalent antioxidant capacity (ABTS/TEAC), cupric ion (Cu^{2+}) reduction antioxidant capacity (CUPRAC), iron ion reducing antioxidant capacity (FRAP), DPPH radical scavenging activity determination and Folin–Ciocalteu methods are the most widely preferred as analytical methods [15–17]. Furthermore, to evaluate and characterize the antioxidant substances in food samples, various analytical methods such as high-pressure liquid chromatography (HPLC) combined with different detection, gas chromatography, micellar electrokinetic capillary chromatography, capillary electrophoresis includes different detection systems and UV–visible spectrophotometry have been used [18–20]. However, these classical methods have great shortcomings for fully validated analyzes such as long pretreatment, need for too much solvent, expensive equipment, long analysis time. They do not provide the necessary procedures for green chemistry, especially due to the use of too much solvent and too much waste in antioxidant analyses. For these reasons, scientists have turned to alternative methods for antioxidant quantification in food samples. Especially in recent years, they have focused on electrochemical techniques which are fast, inexpensive, reliable, non-pre-treatment, and environmentally friendly in the analysis of drugs, pesticides, metal ions and organic molecules such as antioxidants, vitamins and nucleic acid [21–23].

In this chapter, the applicability, sensitivity and reliable maintenance of electrochemical methods, which have attracted great attention in food and food samples, have been examined for the analysis of antioxidants. Moreover, which types of electrochemical methods are used and what advantages they provide have been

investigated for the antioxidant sensing in food samples. It also describes the classification of each used in electrochemical methods by working electrode type, dynamic operating range, the limit of detection (LOD), measurement limit (LOQ), sample type, and standard analyte, etc. While many articles referenced for determining antioxidants by electrochemistry have gained momentum in the literature in the last two decades, we focused our study on the studies conducted in the last 4 years.

2. Electrochemistry

Electrochemistry is the branch of science which is investigating the physical and chemical changes coming from the interaction of the material with electrical factors such as current, potential, and electron charge. Electroanalytical chemistry is based on measuring the electrical properties of solutions containing analytes and switching to quantification using measured electrical signals a collection of electrochemical methods. Moreover, electroanalytical measurement methods are based on two basic points: potentiometric (static methods) and potentiostatic (dynamic methods). Electrode systems in both methods are immersed in the solution containing the analyte, called the electrochemical cell. Potentiostatic methods are widely used for routine analysis because they are less costly, high sensitive, and selective and have wider potential application areas than other electroanalytical methods. The basic principle of these methods is to measure the current that occurs during the oxidation or reduction of the analyte in the chemical reaction.

Electrochemical methods began with the Czech chemist Jaroslav Heyrovsky, discovering the basis of polarography in 1922 and took an important place among the analytical methods. Especially, since the 1980s, it has been possible to develop electrodes that have been modified mechanically or chemically with improved technology. In modification processes, polymers, organic ligands, inorganic clays, phthalocyanines and nanoparticles have been commonly used for the detection of electroactive substances in very small volume complex samples such as biological, environmental and human bodies. In the last twenty years, even very small quantities of substances that are electroactive have been additionally analyzed at high precision, selective by electrochemical methods by carbon-based or modified electrodes have wonderful properties. Electroanalytical methods have also an important place in quantification as well as in obtaining details such as determination, adsorption, reaction rate and equilibrium constants of the number of electrons transferred in the reduction or oxidation electrode reactions. In short, electroanalytical methods provide details on direct or indirect quantitative and qualitative analysis of electroactive species such as antioxidants, drugs, pesticides, etc.

2.1 Voltammetric application for the determination of antioxidant capacity

Voltammetry is a potentiostatic assay based on the recording of the peak current at controlled potential variation by the oxidation or reduction which enables qualitative and quantitative analysis by means in electrochemical reactions. Over the last two decades compared to other electroanalytical techniques, voltammetry has been intensely curious in all the electroanalytical methods due to their are used to analyze numerous compounds by anodic or cathodic scanning and to investigate their conceptual basis of electro-mechanism. There are four voltammetric techniques including cyclic (CV), linear (LSV), differential (DPV), and square (SWV) are commonly used to determination of antioxidant-type compounds.

Voltammetric techniques are an alternative analytical method, proved to have an excellent correlation compare with another conventional analytical process, for a while to study the AC in various food and beverage samples. They can be a benefit to characterize which species compounds have a greater contribution to the antioxidant capacity present for the real samples in terms of quantitative and qualitative by controlled the half-wave peak potential, peak current and the electron transfer number in reaction. The antioxidant capacity is related to the peak currents of oxidation species caused by hydroxyl groups (–OH) and antioxidant species contains many hydroxyl groups. They commonly give an electro-oxidation broad peak at a range of 400 mV- 600 mV depend on pH. So that, almost all antioxidant substances have electro-activity compounds and their peak current and peak potential provide quantitative and qualitative details, respectively. Further, the voltammetric techniques allow investigating the electrochemical behavior of antioxidant agents and interaction with oxygenated species.

Voltammetric methods have gained an important place among determinations of the antioxidant capacity in the last decade. Moreover, due to their great superiority, the use of complex samples such as food and beverages they have become widespread and widely found in the literature. Among these electroanalytical methods, square wave stripping, different pulse stripping, and cyclic voltammetric techniques are the most commonly preferred for the analysis of antioxidants by accuracy and precision. From past to these days, the compounds used as standard agents for the evolution of the AC by studies electrochemical methods are apigenin, ascorbic acid, caffeine, catechin, chlorogenic chrysin, p-coumarin acid, eugenol, fisetin, gallic acid, kaempferol, luteolin, morin, quercetin, rutin, t-resveratrol, Trolox and Malvidin-3-glucoside. As far as we have examined the literature, scientists have however preferred ascorbic acid, caffeic acid, gallic acid, catechin, rutin and quercetin which are often used as antioxidant standard substances due to excessive availability of these substances in food and drink. The chemical structures of some antioxidant molecules are given in **Figure 1**.

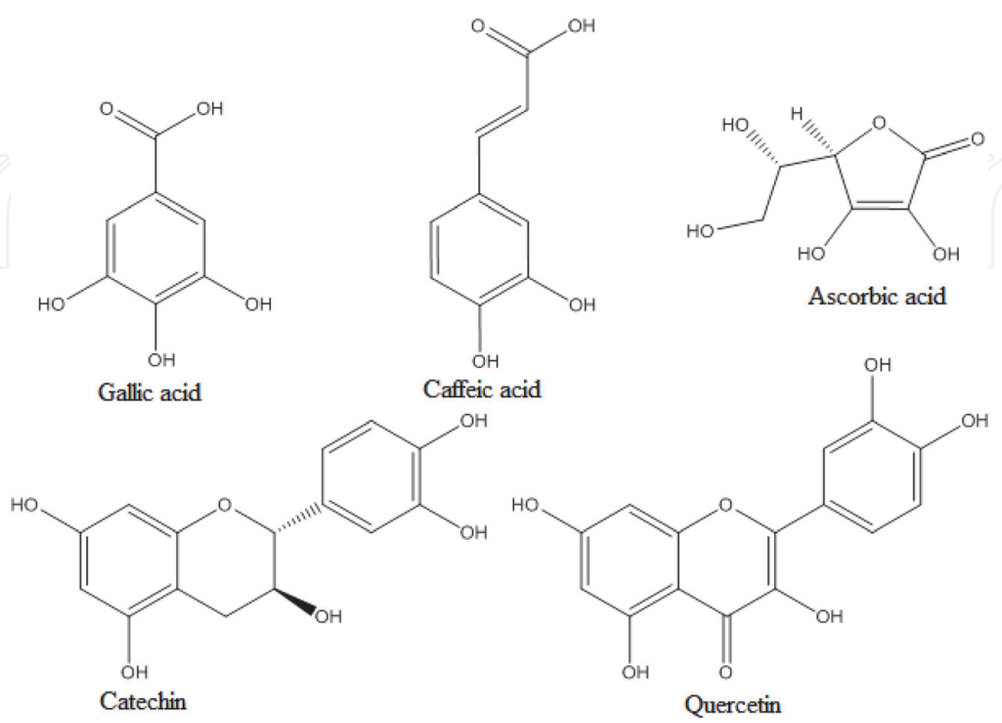

Figure 1.
Molecular formulas of commonly used antioxidants.

2.1.1 Cyclic voltammetric technique

Cyclic voltammetry (CV) is usually the first experiment in the electrochemical operation of a compound in biological materials as nature samples to get in details about the electro-behaviors. In particular, to study the thermodynamics, kinetic, electron transfer, substance transfer type, and as well as quantitative determinations of oxidation or reduction processes can be carried out by cyclic voltammetric technique. In addition to taking a single measurement with CV, sequential multiple measurements can be taken. The most common applications of cyclic voltammetry are additionally electro-polymerization, electrochemical characterization, and the design of modified electroanalytical systems. Two types of cyclic voltammograms can be obtained as irreversible or reversible, depending on the chemical components of the target molecules. In reversible voltammetry, there is a difference of about 59 mV between the reduction and oxidation peak potentials (**Figure 2**).

During the past years, cyclic voltammetry has been used as an alternative to existing methods to evaluate the antioxidant sensing in natural samples such as teas, biological fluids, beverage juices plants, foods and beverage juices on different working electrodes. The most using parameter is peak current because of its proportional to the concentration of the antioxidants. Peak current heights also provide quantitative information about the amount of antioxidant capacity in food samples. The carbon-based working electrodes such as glassy carbon electrode (GCE), carbon paste electrode (CPE), screen printed carbon electrode (SPCE), and modified electrodes (Nanoparticle/GCE, Nanoparticle/CPE, Fe_3O_4/GCE) have been widely preferred in electrochemical measurements for the analysis of total antioxidant capacity (TAC). Peak current and peak potential values of standard substances such as ascorbic acid, caffeic acid, catechin, coumarin, gallic acid, morin, quercetin and rutin were commonly taken care of for the evaluation of TAC. The amount of antioxidants in food samples is generally given as equivalent gallic acid, equivalent value quercetin, etc.

Even though the CV method raises doubts about sensitivity, it also has great advantages. Quick, simple, low detection limit, cheaper and easier application are

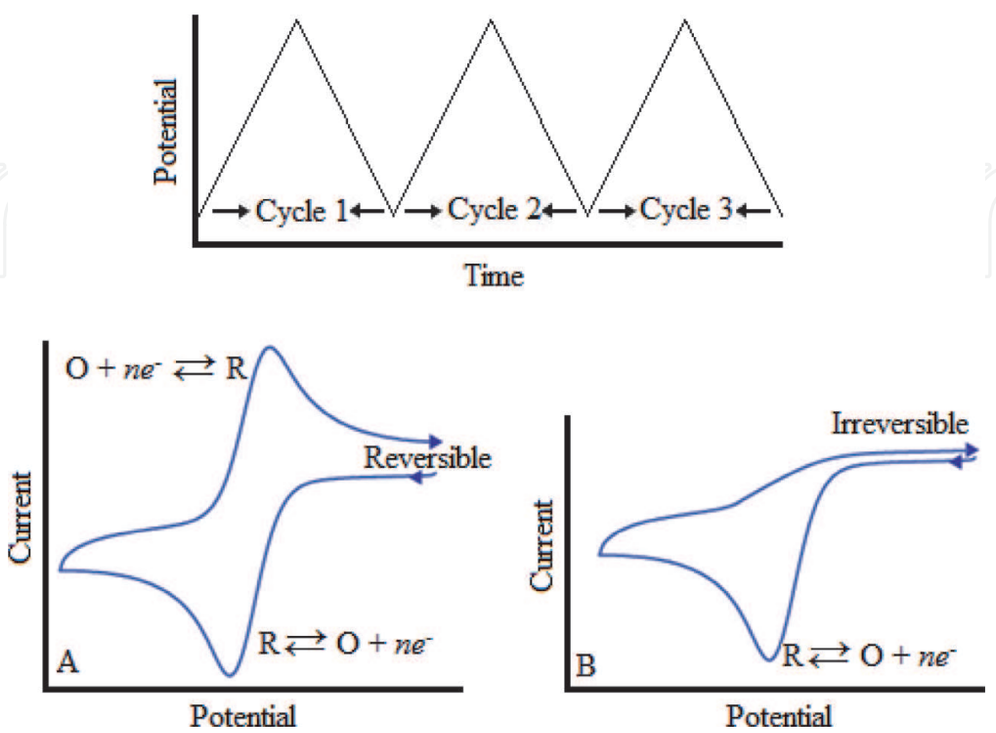

Figure 2.
Potential-excitation signal and voltammograms for the cyclic voltammetry in details.

summarized as great advantages. Interferences effect on antioxidant capacity by a non-antioxidant agent to reducing TAC and non-selective to a family of molecules between carotenoids and polyphenols unless the electrode is modified are drawbacks properties. Despite all of these disadvantages, CV attracts a great deal of attention among analytical methods, and a large number of studies deal with CV are also being undertaken. A large part of the work done up to day time to determine the antioxidant capacity by the CV method is summarized in **Table 1**. **Table 1** includes the type of working electrode, working range, the limit of determination (LOD), the limit of quantification (LOQ), measurement parameter, standard compound and food sample.

2.1.2 Square wave voltammetric technique

Square wave voltammetry (SWV) can be used to perform a faster experiment than other voltammetric techniques. Commonly when the scanning speeds of other techniques are of 1–10 mV/second or more, in the square wave voltammetry a scanning speed is used at 1 V/second. Thus, the target molecule can be analyzed more quickly by SWS. The square wave voltammetry can combine with the stripping technique. Thus, a stripping voltammetric technique was developed to determine electroactive substances at high sensitive enables in ultra-trace concentration levels. Especially, ultra-trace target substances in complex samples can be analyzed by combining the technique with the enrichment stripping process. The working principle of the stripping technique is the same as square wave voltammetry and only two new parameters are more applied as the accumulation time and the accumulation potential (**Figure 3**).

Nowadays SWV and square wave stripping voltammetry (SWSV) are frequently applied to deduce compounds such as drugs, heavy metals, pesticides and antioxidants, etc. in numerous specimen types because they have excellent analytical sensitivity and selectivity. Furthermore, SWV and its derivate combined technique can be applied for simultaneous determination of compounds which are close oxidation or reduction peak potentials like paracetamol, ascorbic acid, uric acid and dopamine. In the last decade, SWV and SWSV have been more effective in determining antioxidant substances in the complex matrix samples and are superior compared with analytical methods especially spectrophotometric to evaluate quantification and qualification. It is one of the most important electroanalytical methods for the determination of antioxidants since it is a wide working range, low detection limits, easy to apply, cheap and non-pretreatment. Furthermore, they have been successfully analyzed the phenols in food samples which is called a type of important antioxidant such as o-phenylenediamine, p-chlorophenol, p-aminophenol hydroquinone, pyrocatechol and phenol, etc. At the same time, various antioxidant substances such as gallate, gallic acid, quercetin and caffeine were easily studied in food or beverage samples at high precision, accuracy and selective on the carbon-based electrode. Besides, at nM concentration of antioxidant substances comparable to chromatographic techniques have been determined by modified electrodes which are increasing conductivity accurately and selectively in tea samples. Evaluation of antioxidant capacity by SWV or SWSV techniques in the last 4 years are summarized in **Table 2** according to the type of working electrode, working range, the limit of detection (LOD), quantity limit (LOQ), measurement parameter, standard composition and food sample.

2.1.3 Differential pulse voltammetric technique

Differential pulse voltammetric technique (DPV) is one of the most widely used for the analysis of both organic and inorganic species. Pulse voltammetry

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
CV	Pt electrode	juglone (5-hydroxy-1,4,-naphthoquinone)	—	—	—	walnut	—	2.1 V	—	[24]
CV	GCE	polyphenols	—	—	—	Black Tea Samples *Camellia sinensis*	pH 7.0 (PBS)	+ 0.5 V	Catechin, gallic acid	[25]
CV	Graphite Paste Electrode	Rutin (RT)	200–1000 μM	89,4 μM		pharmaceutical sample (Captopril)	pH 4.0 (PBS)	+ 0.44 V	—	[26]
CV	Nanotuned Gold Nanoparticles and Solvothermally Reduced Graphene modified GCE (GCE/EAuNPs4 /rGO/ Naf.)	sinapic acid (SA)	20 μM - 200 μM	33.43 (±0.21) nM		Human urine samples	pH 7.6 (PBS)	0.47 V	L-cystine, glycine, alanine, serum albumin, uric acid, citric acid, ascorbic acid, and urea	[27]
CV	glassy carbon electrode	caffeic acid, chlorogenic acid, quercetin, gallic acid, (+)-catechin, ascorbic acid	—	—	—	Apricot pomace extracts	pH 4 acetate buffer	0.51 V	—	[28]
						black currant pomace extracts		0.54 V		
						Grape pomace extracts.		0.48 V		
CV	glassy carbon disc electrode	Tannins	—	—	—	wine solution	—	—	—	[29]
CV	glassy carbon electrode	polyphenols and flavonoids	—	—	—	Venezuelan propolis	pH 7.00 (PBS)	−0.90 V (cathodic) −0.75 V (anodic)	—	[30]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
CV	carbon paste electrode	Trolox	—	1.9 μM	0.6 μM	red wine, coffee and green tea	pH 7.0 (PBS)	—	—	[31]
CV	Carbon Paste Electrode (CPE)	Quinizarin (H2Qz)	0–36 μM	3.129 ± 1.200 μM	10.429 ± 1.133 μM	—	pH 7.00 (Aqueous)	—	Anthrarufin (H2Arf), Chrysazine (H2Cz), Anthraflavin (H2Afv)	[32]
CV	glassy carbon electrode (GCE)	polyphenols	—	—	—	Malaysian honey	pH 7 (PBS)	—	glucose and fructose	[33]
CV	ZnO nanoflowers modified carbon paste electrode	p-nitrophenol (p-NP)	0.1–1 μM	0.08 μM	—	Astragalus membranaceus	pH 7.0 (PBS)	—	—	[34]
CV	carbon nanotube (CNT)-carboxymethylcellulose (CMC) electrode MWCNT-CMC/Au	Curcumin	1.0–48 μM	0.21 μM	—	Real samples	pH 6.0 citric acid	0.30 V	—	[35]
CV	GCE	polyphenols, tannins, flavonoids, and sterols/ triterpènes.	—	—	—	*Thymus vulgaris*	pH 7 (PBS)	—	—	[36]
CV	carbon screen printed electrode (cSPE)	Ethoxyquin (EQ)	20–100 mM	7.5 mM	20.0 mM	Salmon Samples	pH 3.5 ammonium formate buffer	+0.45 V	BHA, BHT, diphenylamine, and ascorbic acid (AA)	[37]
CV	carbon nanotube (CNT)-carboxymethylcellulose (CMC) electrode	monohydroxycinnamic acid	1.0–194 μM	0.071 μM	—	real food samples	pH 6.0 citric acid	—	—	[38]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
CV	CPE	catechol, (CAT)	30.0–540 μM	2.47 μM	8.24 μM	wine and food samples	pH 7.4 (PBS)	0.24 and 0.46 V	—	[39]
		4-ethylcatechol (4-EC)	10.0–350 μM	0.282 μM	0.339 μM					
		4-ethylguaiacol (4-EG)	1.00–210 μM	0.111 μM	0.371 μM					
	CPME-CNT	CAT	30.0–540 μM	1.37 μM	4.58 μM					
		4-EC	10.0–350 μM	0.184 μM	0.613 μM					
		4-EG	1.00–120 μM	0.106 μM	0.353 μM					
	CPME-AB	CAT	30.0–540 μM	1.85 μM	6.16 μM					
		4-EC	0.20–350 μM	0.0863 μM	0.288 μM					
		4-EG	1.00–120 μM	0.0937 μM	0.312 μM					
CV	HP-ZnO/GCE	Gallic Acid (GA)	0.1–130 μM	0.02 μM	—	Wine sample	pH 3.0 (PBS)	+0.59 V	catechol (CT), dopamine (DA), caffeic acid (CA), morin (MR), hydroquinone (HQ), uric acid (UA), ascorbic acid (AA), ferulic acid (FA)	[40]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
CV	glassy carbon electrode/poly(3,4-ethylenedioxythiophene)-gold nanoparticles-sinusoidal voltage (GC/PEDOT-AuNPs-SV)	caffeic acid (CA)	10 μM - 1 mM	4.24 (±0.12) μM	—	juice samples (like peaches and apple juices)	pH 7 (PBS)	—		[41]
CV	carbon electrodes	piperine	5 mM	—	—		pH 1.2 $HClO_4$			[42]
CV	Poly(3,4-ethylenedioxythiophene)-tyrosinase PEDOT-Tyr	Caffeic acid (CA)	10–300 μM	4.33 μM	14.43 μM	Wines and beers	0.1 M H2SO4	0.22 V	—	[43]
CV	glassy carbon electrode (GCE)	Catechin	0.1 mM	—	—	grape skin and seed	pH 3.6 tartaric acid buffer	483 mV	—	[44]
		Caffeic acid						445 mV		
		Gallic acid						472 mV		
		Oenin chloride						652 mV		
		Rutin						260 mV		
CV	Single Walled Carbon Nanotubes modified Screen Printed Carbon Electrodes (SWCNT-SPCE)	Catechin	0.1 mM	—	—	grape skin and seed	pH 3.6 tartaric acid buffer	132 mV	—	[44]
		Caffeic acid						139 mV		
		Gallic acid						122 mV		
		Oenin chloride						377 mV		
		Rutin						201 mV		

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
CV	Carbon nanofibers CNF	Caffeic acid (CA)	0.1–40 μM	3,23 nM	10,77 nM	Active Detox, DVR-Stem Glycemo, and green tea	pH 3.6 (PBS)	—	uric acid, ferulic acid, vanillic acid, gallic acid, and catechol	[45]
CV	Graphene/Neutral Red -GCE	UA	0.5–50 μM	0.076 μM	—	human urine and blood serum sample	—	—	urine and blood serum samples	[46]
CV	PEDOT(poly(3,4-ethylenedioxythiophene) /GCE	UA	6–100 μM	7 μM	23 μM	milk sample	pH 6.6 (PBS)	—	A-lactose, L-aspartic acid, L-glutamic acid, L-histidine	[47]
		AA	30–500 μM	45 μM	149 μM			—		
CV	ZnO-graphene/ ITO	UA	5-80 μM	5.0 μM	—	—	1 M H_2SO_4	—	AA	[48]
CV	GOx-chitosan /Co3O4/ Au- graphene transistors (GOx-CHIT/Co3O4 modified SGGT)	UA	0,3-3 μM	0.1 μM	—	real tear samples	PBS	—	AA, Fructose, Xylose, Mannose	[49]

Table 1.
Evaluation of antioxidant capacity by CV technique.

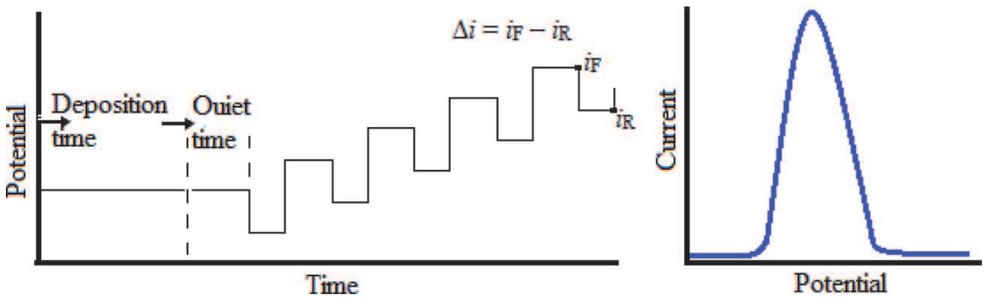

Figure 3.
Potential-excitation signal and voltammogram for the square wave stripping voltammetry in details.

techniques were proposed by Baker and Jenkin in 1952 as a more sensitive measurement electroanalytical method. Differential pulse voltammetry techniques can be used to determine up to 10^{-8} M concentration of the target agents. The peak current (I_p) is a function of the concentration for the electroactive species and is linear as $Ip = f$ (C). Also, it is possible to analyze substances not only quantitative analysis but also qualitative analysis with pulse technique. The peak currents are related to the concentration of the substance whereas the peak potential values are related to the selectivity. Thus, simultaneous determinations of the substances have been studied by DPV on bare or modified electrodes (**Figure 4**).

Nowadays, quite a lot of DPV studies can be found in the literature for the very sensitive detection of heavy metal, drug, pesticide, antioxidant agent and inorganic/organic species on numerous bare and modified working electrodes. Besides, DPV is one of the most important candidates to determine the trace amount of target agents in analytical methods due to its high sensitivity and selective. Also, it can be applied to complex samples as biological and food samples such as blood and serum, beverages. Especially, DPV has an important place among antioxidant determination methods because of these advantages and the availability of low concentration.

In recent years, DPV has been used frequently in determining the total antioxidant capacity without any pretreatment of solid and liquid food samples. The complex matrix such as biological and food samples contain very dense different types of substances. For this reason, despite it is indeed very difficult to selectively and precisely determine the antioxidant capacity in some complex matrixes; DPV is the most applicable method for such species. There are also plenty of studies were published which deal with chlorogenic acid, caffeic acid, p-coumaric acid, quercetin, gallic acid and ferulic acid, etc. as illustrating the antioxidant properties were determined by DPV on bare or modified electrodes based on carbon nanomaterials. Several applications, based commonly on the used as a determination of antioxidant capacity are given in **Table 3**.

In amperometric techniques, the current produced during the reduction or oxidation of an electroactive species at a constant potential value that is applied between a working electrode and reference electrode is measured, in this way providing specific quantitative electroanalytical knowledge for the target analyte. Especially, amperometric, which is based on electrical current analysis, is commonly utilized in microchip electrophoresis applications owing to its high sensitivity, it also lets for the determination of electroanalytical active species without derivatization, accomplishing adjustable versatility and selectivity (**Table 4**).

Ganesh et al., synthesized zinc oxide nanoparticles using mechanochemical synthesis technique. New ZnO nanoparticle as hexagonal prism was investigated by scanning electron microscopy, X-ray diffraction, particle size distribution, ultraviolet–visible spectroscopy, and energy-dispersive X-ray spectroscopic methods. Electrochemical properties of the newly prepared electrode were characterized by using an amperometric method and cyclic voltammetry technique. The prepared electrode has

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
SWV	glassy carbon electrode modified with graphite/ bismuth (III) oxide (Gr/ Bi_2O_3/GCE)	Ellagic acid (EA)	—	0.07 nM	0.21 nM	walnut and pomegranate	pH 3.0 (BRB)	0.6 V	inorganic ions (Na^+,K^+,Ca^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}), Glucose, Fructose, Eugenol, Capscasin	[50]
SWV	CPE/PAG	quercetin (QRT)	0.099–1.090 μM	0.029 μM	—	crude natural fruits (orange, apple and onion)	pH 6.0 (PBS)	0.18–0.22 V (ox and red)	Aspartic acid (ASP), Gallic acid (GAL), Sucrose (SUC) and Tartaric acid (TAC)	[51]
		rutin (RT)		0.058 μM				0.31–0.30 V (ox and red)		
SWV	$TPCo_3O_4$&SWCNT@CPE	α-lipoic Acid	2–100 μM	0.37 μM	—	dietary supplements	pH 6 (BRB)	—	Vitamins (vitamin C, B2, and B6), possible ingredients in LA pharmaceutical formulations	[52]
SWV	pencil graphite electrode	naringenin (NGN)	75 nM-0,1 mM	44 nM	0,111 μM	Citrus juice, fruits and peel	pH 4.00 (KHPT)	—	—	[8]
SWV	Single-Walled Carbon Nanotube Modified Glassy Carbon Electrode (SWCNT/GCE)	Quercetin (QCT)	0.01–100 μM	0.007 μM	—	tea samples (tea:green, basil and black)	pH 5.0 (PBS)	—	—	[53]
SWV	Untreated boron doped diamond electrode (BDDE)	Sesamol	0.2 mM–1.0 mM	85 nM	—	tahini halva samples	pH 2.0 H_2SO_4	—	Cu^{2+}, Pb^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, K^+, Cl^-,and ascorbic acid and catechol, glucose, and fructose	[54]
SWV	immobilization (in solution) of laccase onto the activated carboxylic groups of carboxymethyl-botryosphaeran (CMB).	Quercetin (QCT)	0.0498–0.794 μM	0.026 μM	—	Red wine Green tea Apple juice Lemon juice	pH 6.0 (PBS)	0.23 V	epinephrine, dopamine, paracetamol, guaiacol and catechol, uric acid and inorganic ions (Ca^{2+},Mn^{2+}, Fe^{2+}, Zn^{2+},SO_4^{2-} and NO_3^-)	[55]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
	(CBPE-CMB/LCE) biosensor									
SWV	CNF-ZnO modified glassy carbon electrode (CNF-ZnO-GCE)	Silymarin	2–123 nM	1 nM	—	Human serum samples and urine samples were	pH 7.0 (PBS)	+0.20 V	NO_3^-,Na^+, Cu^{2+}, K^+, 4-nitrophenol, rutin, dopamine, caffeic acid, luteolin, tetracycline, hydrogen peroxide, glucose, ascorbic acid, epinephrine, uric acid, and quercetin	[56]
SWV	gold nanoparticle/graphene quantum dots (AuNP/GQD) nanozyme–modified screen-printed carbon electrode (AuNP/GQDs/SPCE)	Quercetin	0,1 nM - 1 mM	0,033 nM	0,1 nM	Human plasma	pH 5 (BRB)	—	glucose, sucrose, ascorbic acid, riboflavin, phenylalanine, L-tryptophan, L-tyrosine, bisphenol A, lysine, uric acid, and two metal ions such as Na + and Co2+	[57]
SWV	SWCNTs-SPCE	Polyphenols (caffeic acid, gallic acid, catechin and malvidin-3-glucoside	—	—	—	Wine samples	pH 3.6	—	—	[10]
SWV and AdSV	boron-doped diamond electrode (CPT-BDDE)	5-O-Caffeoylquinic acid (5-CQA)	2.8 μM - 0,17 mM	0.4 μM	—	Food&beverage samples (vanilla-enriched instant coffee, vanilla sugar, cola soft drink)	0.1 M HNO3	0.68 V	caffeic acid, p-coumaric acid, gallic acid, ferulic acid, sinapic acid, and syringic acid, K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, NO_3^-, Cl^- and SO_4^{2-}	[58]
		vanillin (VAN)	3.3 μM - 0,33 mM	0.38 μM				1.15 V		
		caffeine (CAF)	0.52 μM - 0,21 mM	0.15 μM				1.50 V		

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
SWASV	Gold disk	Cu(II) and TBHQ	5.66–113.37 μg/kg 4.76–92.40 mg/kg	0.351 μg/kg 1.13 mg/kg	—	—	pH 2 (BRB)	—	—	[59]

Table 2.
Evaluation of antioxidant capacity by SWV or SWSV.

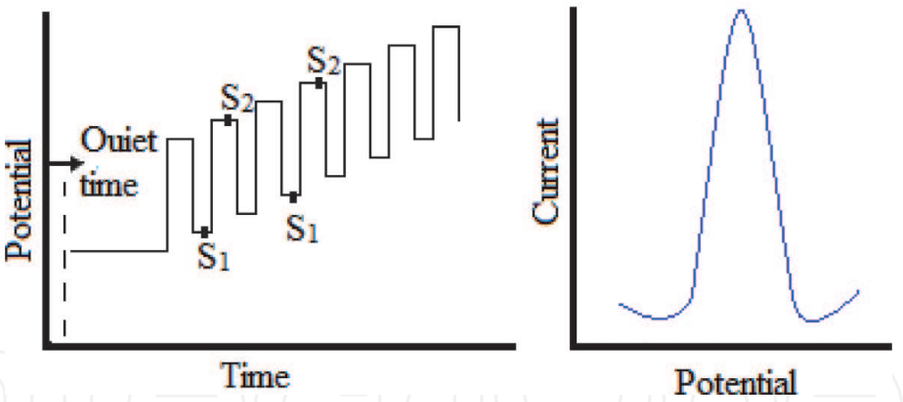

Figure 4.
Potential-excitation signal and voltammogram for the differential pulse stripping voltammetry in details.

a wide working linear range between 0.1–130 μM with a detection limit of 0.02 μM. Obtained results showed that the prepared electrode has numerous active surface sites, good electronic activity, and surface area. They applied the proposed electrode to the determination of gallic acid in samples as wine successfully [40].

Kumar and coworkers successfully synthesized NiO nanoparticles from natural fruit using an efficient, simple, and low-cost technique. The obtained NiO nanoparticles were investigated with various methods such as FTIR, XRD, TEM, SEM, UV, and PL. XRD studies showed that NiO nanoparticles have cubic geometry. The band of Ni-O bond was shown at 430 cm^{-1}. Photocatalytic properties of the obtained NiO nanoparticles were applied to photodegrade the methylene blue dye. They used the prepared electrode to the determination of dopamine with the LOD of 11 μM [93].

Koçak et al. prepared a new composite electrode using carbon nanotube and poly-l-methionine onto the glassy carbon electrode. Electrochemical properties and surface structure of the prepared electrode were studied using electrochemical impedance spectroscopy and scanning electron microscopy. Electrochemical properties of gallic acid with the proposed electrode were investigated in various techniques such as differential pulse voltammetry, cyclic voltammetry and amperometry. The obtained results of electrochemical studies exhibited that the prepared electrode shows a suitable method of determination for gallic acid in pH 2.2 BR buffer solution. The prepared sensor has a wide working linear range with two linear segments between 4 nM-1.1 μM and 1.7–20.0 μM with LOD of 3.1 nM. They used the prepared new sensor for the detection of gallic acid in various samples as black tea, green tea and wine samples. The experimental results showed that the proposed sensor exhibit high selectivity, reproducibility, stability and catalytic effect [88].

Potentiometry is an electrochemical technique based on measuring the potential difference between two electrodes called working and reference electrodes. The working basis of the potentiometry technique is the potential difference based on the concentration of an analyte in the sample solution relative to a reference electrode (**Table 5**).

Brainina and coworkers developed a new, simple, reliable and fast potentiometric method for the determination of plant total antioxidant activity. Plant micro suspension and extracts were analyzed by the proposed method. The experimental conditions for acquiring plant extracts were selected for the highest antioxidant activity as extraction time 20 min at +80°C. The characterization of plant micro suspensions reduces the duration of plant total antioxidant activity evaluation. Comparison of the obtained results of antioxidant activity of green tea and black tea micro suspensions samples with the results of the investigations of extracts prepared by a certified method showed no difference [95] (**Tables 6** and 7).

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPV	GCE/PoPD/Pt	Rosmarinic acid (RA)	3 μM – 7 μM	0.9 μM	—	Melissa officinallis, Rosmarinus officinals	pH 2 H_2SO_4	0,63 V	phenolic compounds-caffeic acid, ascorbic acid, coumaric acid, 2,5 dihydroxybenzoic acid, chlorogenic acid, rutin, and gallic acid	[60]
		protoca-techuic acid (PCA)	2 μM – 70 μM	0.8 μM	—			0,53 V		
DPV	ZrO2NPs-AuNPs- DES/ CPE	Caffeic acid (CA)	0.22–55 μM	25 nM	—	green tea and fruit juices	pH 3 (BRB)	—	—	[61]
DPV	Fluorine doped graphene oxide/GCE	Caffeic acid (CA)	0.5–100.0 μM	0.018 μM		wine	pH 2.65 (BRB)	—	p-coumaric acid, hydroquinone, trans-ferulic acid, gallic acid, glucose, and ascorbic acid	[11]
DPV	CuO nano-rice/ GCE	UA	1–160 μM	1.2 μM	—	real samples of dopamine injection, human serum, and urine samples	pH 7 (PBS)	—	Glucose, Fructose, Galactose	[62]
		DA	1–150 μM	0.42 μM	—			—		
DPV	Poly(DPA)/SiO_2@ Fe_3O_4/CPE	UA	1.2–8.2 μM	0.4 μM	1.2 μM	Fresh human serum samples	pH 7.0 (PBS)	0.3 V	Sucrose, DA, AA, Glucose, Folic acid	[63]
DPV	Carbon paste modified with Bi decorated multiwalled carbon nanotubes and cetrimonium bromide (CTAB)	Caffeic acid (CA)	0.06–500 μM	0.157 nM	1.910 nM	Coconut water, coffee, tea	pH 7.0 (PBS)		AA, UA, FA, Trp, Mor, GA, Glucose and FoA	[64]
DPV	Bimetallic $CoFeSe_2$ nanosphere in functionalized carbon nanofibers $CoFeSe_2$/f-CNF	Caffeic acid (CA)	0.01–263.96 μM	0.002 μM	—	Red wine samples by	pH 7.0 (PBS)	0.21 V	catechol (CC), hydroquinone (HQ), epinephrine (EP), dopamine (DA), uric acid (UA), and ascorbic acid (AA)	[65]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPV	Carbon/iron-based active catalyst f-MWCNTs/a-$NaFeO_2$	Caffeic acid (CA)	0.1–17.2 μM	0.002 μM	0.0068 μM	coffee, green tea, red wine	pH 7.0 (PBS)	—	catechol (CT), gallic acid (GA), ascorbic acid (AA), hydroquinone (HQ), and uric acid (UA)	[66]
DPV	N-doped carbon quantum dots/hexagonal porous copper oxide decorated multiwall carbon nanotubes N-CQD/HP-Cu_2O/ MWCNT/GCE	Caffeic acid (CA)	0.05–43 μM	0.004 μM	—	red wine samples	pH 7.0 (PBS)	—	dopamine (DA), catechol (CC), ascorbic acid (AA), uric acid (UA) and epinephrine (EP)	[67]
DPV	Ce-TiO_2/carbon nanotube composite Ce-TiO_2/CNTs	Caffeic acid (CA)	0.001 -10 μM	0.0003 μM		caffeic acid tablets samples	pH 6.0 (PBS)	—	Cl^-, Br^-, $SO4^{2-}$, $NO3^-$, $H_2PO_4^-$, Na^+, K^+, Mg^{2+} and Al^{3+}, glucose, L-serine, uric acid, urea, oxalic acid, glycine, alanine, L-cysteine, L-tyrosine, L-glutamic acid, and guanidine acid	[68]
DPV	MOF-818 metal–organic framework-reduced graphene oxide/ multiwalled carbon nanotubes composite MOF-818/ RGO/MWCNTs/GCE	caffeic acid (CA), chlorogenic acid (CGA), and gallic acid (GA)	0.2–7 μM 7–50 μM	5,2 nM	—	human serum and urine samples	pH 3.0 (PBS)	—	Na^+, K^+, SO_4^{2-}, Cl^-, 40-fold glutamic acid, glycine, glucose, sucrose, urea, ascorbic acid, uric acid, and equal concentration of baicalein, luteolin, and vanillic acid	[69]
DPV	Fe_3O_4 @ZIF-4 nano-hybrid on a glassy carbon electrode (GCE) (Fe_3O_4 /GCE, ZIF- 4/ GCE)	p-coumaric acid (CA)	0.50–12.00 μM	0.18 μM	0.60 μM	orange juices samples	pH 4 (BRB)	0.71 V	anions, cations and other polyphenols such as SO_4^{2-}, NO_3^-, Cl^-, Fe^{3+}, Fe^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, Li^+	[70]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
									ions, citric acid, glucose, catechin and quercetin	
DPV	graphene modified screen-printed electrode	Melatonin	—	0.03 mg/L	—	food supplements	pH 7.4	0.268 (±0.014) V	—	[71]
DPV	multi-walled carbon nanotubes modified carbon paste electrode (MWCNTs/CPE).	quercetin (QU)	—	1.96 nM	—	Orange juice	pH 2.0 (BRB)	—	tannic acid (TA)	[72]
DPV	—	polyphenols	—	—	—	Black Tea Samples Camellia sinensis	pH 5.5 (PBS)	+ 0.5 V	Catechin, gallic acid	[25]
DPV	screen printed carbon electrode	gallic acid	0.1–2 mM	23–103 μM	70–310 μM	White wine Green tea Apple juice	pH 5.8; 7; 8 (PBS)	—	caffeic and ascorbic acid	[73]
DPV	alumina-modified glassy carbon electrode GCE	Caffeic Acid (CA)	0.1–5 μM	0.004 μM	0.01 μM	Tea (Green, Black, Mint, Hibiscus, Rosemary), wine and phytotherapics	0.1 M $HClO^4$	0.519 ± 0.002 V (Green tea) 0.528 ± 0.002 V (Black tea) 0.526 ± 0.001 V (Mint tea) 0.533 ± 0.002 V (Hibiscus tea) 0.508 ± 0.001 V (Rosemary tea) 0.571 ± 0.005 V (Phytotherapic) 0.532 ± 0.001 V (Wine 1) 0.525 ± 0.002 V (Wine 2)	—	[74]
		Gallic Acid (GA)	0.1–5 μM	0.005 μM	0.02 μM					
		Catechin	0.1–5 μM	0.001 μM	0.003 μM					
		Quercetin (QCT)	0.1–15 μM	0.005 μM	0.02 μM					

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPV	nanoporous gold electrodes (NPG)	ascorbic acid (AA)	0.32 to 3.4 mM	63 μM	—	mimic human serum sample of fetal bovine serum	pH 7.4 (PBS)	0.05 V	—	[75]
		uric acid (UA)	0.065 to 1.5 mM	9.0 μM				0.35 V		
DPV	glassy carbon electrode (GCE)	Gallic Acid (GA)	19.92–98.04 ppm	—	—	mango (pulp, peel, and seed)	pH 5 (BRB)	0.445 and 0.550 V (oxidation peaks)	0.05 V	[76]
		Trolox	2.34–472.18 μM							
DPV	CoSe2@rGO modified SPCE	propyl gallate	0.075–460.15 μM	16.35 (±0.46) nM	—	spiked meat samples (Chicken, Beef)	pH 7.0 (PBS)	0.34 V	uric acid (UA), ascorbic acid (AA), dopamine (DA), hydroquinone (HQ), catechol (CT), epinephrine (EP), and norepinephrine (NEP)	[77]
DPV	Nano-Graphene-platelets (nGp)- Brilliant green (Bg)/Modified carbon paste electrode (nGp- Bg/MCPE)	Hesperidin (HES)	0.1–7.0 μM 7.0–100.0 μM	50.0 nM	—	Fortified Fruit Juice Samples (lemon juice, orange rind, and peppermint extract that contain HES)	pH 7.5 (PBS)	—	AA, Bioflavonoids (such as quercetin, rutin, naringenin, morin), Inorganic ions (Ca^{2+}, Mg^{2+}, K^{+}, Zn^{+}, Cu^{2+}, Cl^{-}, SO_4^{2-})	[78]
DPV	5-amino-2-mercapto-1,3,4-thiadiazole (p-AMT) on nitrogen-doped carbon sphere (N-CS) modified glassy carbon (GC) electrode p-AMT@N-CS/GC (1) p-AMT@N-CS/GC (simultaneous addition) (2)	Gallic Acid (GA)	5–1187 μM (1) 5–128 μM (2)	0.58 μM (1) 0.82 μM (2)	—	Grape juice samples	pH 7.0 (PBS)	+0.06 V (GA)	ascorbic acid (AA), uric acid (UA), catechol (CC), and hydroquinone (HQ), K^{+}, Na^{+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, NO^{3-}, Cl^{-}, sulfate ion (SO_4^{2-}, and glucose	[79]
		Caffeic Acid (CA)	5–2082 μM (1) 5–128 μM (2)	0.143 μM (1) 0.30 μM (2)				+0.14 V (CA)		

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPV	SWCNT-Subphthalocyanine (CS) Hybrid Material modified GCE electrode (CS/GCE)	catechin	0.1–1.5 μM	13 nM	43 nM	real tea samples (such as green, rosehip fruit, Turkish and Indian black tea)	pH 3 (BRB)	—	metal ions (such as K^+, Na^+, Li^+, Cu^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}), rutin, 6-methoxy flavone, gallic acid, caffeic acid, biomolecules (viz. caffeine, ascorbic acid, citric acid and glucose)	[80]
DPV	Cobalt oxide nanoparticles-modified carbon-paste electrodes (CoO-NPs-CPE)	Gallic Acid (GA)	0,1–1 μM	1.52 μM	—	Red and White Wine	pH 2.0 (PBS)	0.61 V	Metals ions (K+, Cl−, Na+, Fe3+), ascorbic acid and quercetin	[81]
DPV	graphite/chemically modified silica ceramic electrode (SMICl/C)	Quercetin (QRT)	9–102 μM	3.2 μM	—	pharmaceutical "Quercetin"	Ethanol	0.102–0.155 V	—	[82]
			10–100 μM	3 μM			3:2 ethanol/water	0.561–0.571 V		
			13–95 μM	4.4 μM			4:1 ethanol/water	0.561–0.592 V		
			0.15–60 μM	0.46 μM			Water	0.134–0.155 V		
DPV	glassy carbon electrode modified with polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWNT) and poly (pyrocatechol violet) (polyPCV/f-SWNT/GCE)	Gallic acid (GA)	0.75–10 10–100 μM	0.12 μM	0.41 μM	Cognac XO Brandy VS Brandy 5-Star	pH 2.0 (BRB)	0.48 V	K^+, Na^+, Mg^{2+}, Ca^{2+}, NO_3^-, Cl^-, and SO_4^{2-} and glucose, rhamnose, sucrose as well as ascorbic acid, phenolic aldehydes (vanillin, syringaldehyde)	[83]
		Ellagic Acids (EA)	0.75–7.5 7.5–100 μM	0.11 μM	0.37 μM			0.63 V		

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPV	Sodium dodecyl sulfate modified carbon composite paste electrode	Curcumin	0,2 - 1 μM 1.5 - 4.5 μM	27 nM	92 nM	Natural food supplement	pH 6.0 (PBS)	—	Na^+,K^+, Mg^{2+}, Zn^{2+}, ascorbic acid, glucose, starch, tyrosine and tartazine	[84]
DPV	implemented functionalized-MWCNT/ Nileblue- composite on carbon paste electrode (fMWNCT/NB/ MCPE)	Naringenin (NR)	10.0–50.0 μM 0.9–10.0 μM	0.30 μM	0.93 μM	fruit juices(Grape juice, Tomato juice, Orange juice)	pH 7.0 (PBS)	—	AA, GLU, Na^+, Mg^{2+}, K^+, Ca^{2-}, Cl^-, SO^{4-}	[85]
DPV	vitreous carbon electrode	Trolox	50 μM to 600 μM	43.8 μM	120 μM	Greigia sphacelata fruit (Chupón or Quiscal)	pH 7.4 (PBS)	—	—	[86]
DPV	Screen Printed Carbon Electrodes	Polyphenols	—	—	—	Wine	pH 3.20 Tartaric Acid Solutions	—	—	[87]
DPV	Poly(L-Methionine)/ Carbon Nanotube Glassy Carbon Electrode (PLM/ MWCNT/GCE)	Gallic acid (GA)	0.004–1.1 μM 1.7–20 μM	3.1 nM	—	green tea, black tea, and red wine samples	pH 2.2 (BRB)	—	Na^+,K^+,Ca^{2+} Mg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, ascorbic acid, theophylline, caffeine, cysteine, glucose, fructose, sucrose, and glycine	[88]
DPV	pencil graphite electrode	naringenin (NGN)	78,6 nM - 0,182 mM	30,6 nM	102 nM	citrus juice	pH 4.00 (KHPT)	—	—	[8]
DPSV	3D SWCNTs-coumarin hybrid modified glassy carbon electrode (3DSWCNTs- coumarin/ GCE)	Quercetin (QCT)	0.25–3 μM	20 nM	66 nM	Tea samples	pH 2.0 (BRB)		ascorbic acid, caffeine, citric acid, l-cysteine, glycine, glucose, Na^+, Mg^{2+} Ca^{2+}, SO_4^{2-}, NO^{3-} and Cl^-, gallic acid, 6-methoxyflavon	[89]

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
DPAdSV	unmodified screen-printed carbon electrodes (SPCEs)	Capsaicinoids	0.16 - 16.37 μM	0.05 μM	0.15 μM	fresh chili pepper samples (Meiren chili pepper, Chaotian green chili pepper, Chaotian red chili pepper, Xiaomi green chili pepper, and Xiaomi red chili pepper)	0.10 M HCl	0.40 V	Fe^{3+},Cu^{2+},K^{+},Na^{+}, Ga^{2+},Cl^{-},$SO_4{}^{2-}$ and glucose, and 100-fold of Mg^{2+}	[90]
DpAdSV	screen-printed carbon electrode modified with single-walled carbon nanotubes (SWCNTs)) and Prussian blue (PB) coated with chitosan	Rutin	0.03 to 0.24 μM 0.25 to 2.0 μM	0.01 μM	—	black tea, coffee and synthetic drink of tea	pH 3.0 (PBS)	0.25 V (ox) 0.096 V (red)	morin and quercetin	[91]
DPCV	molecularly imprinted poly (p-aminobenzene sulphonic acid) on carbon nanodots coated pencil graphite electrode (FA-imp/CNDs/PGE)	folic acid (FA)	2.2–30.8 ng/mL	2.02 ng/mL		drug tablets and human urine samples	pH 6.2 (PBS)	—	Methotrexate (MTX), folinic acid (FCA), tetrahydrofolic acid (THF), pyridoxine (PYR), and 5-methyltetrahydrofolate (5- THF)	[92]

Table 3.
Evaluation of antioxidant capacity by DPV or DPSV.

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
Amperometry (AMP)	HP-ZnO/GCE	Gallic Acid (GA)	0.1–130 μM	0.02 μM	—	Wine sample	pH 3.0 (PBS)	+0.48 V	catechol (CT), dopamine (DA), caffeic acid (CA), morin (MR), hydroquinone (HQ), uric acid (UA), ascorbic acid (AA), ferulic acid (FA)	[40]
Amperometry (AMP)	Nickel oxide nanoparticles modified glassy carbon electrode (NiO NPs/GCE)	Dopamine (DA)	—	11 μM	—	*Limonia acidissima* natural fruit juice	pH 7.2 (PBS)	0.41 V	—	[93]
amperometry (AMP)	Poly(L-Methionine)/ Carbon Nanotube Glassy Carbon Electrode (PLM/ MWCNT/GCE)	Gallic acid (GA)	0.002–0.1 μM 0.2–12 μM	0.5 nM	—	green tea, black tea and red wine samples	pH 2.2 (BRB)	0.5 V	Na^{+},K^{+},Ca^{2+} Mg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, ascorbic acid, theophylline, caffeine, cysteine, glucose, fructose, sucrose, and glycine	[88]
Amperometry	GCE/PoPD/Pt	Rosmarinic acid (RA)	1 μM – 55 μM	0.5 μM	—	Melissa officinallis, Rosmarinus officinals	pH 2 H_2SO_4	—	—	[60]
		protoca-techuic acid (PCA)	1 μM – 60 μM	0.6 μM	—			—		
Chronoamperometry (CA)	Graphite/Lacc–PDA	gallic acid	1–150 μM	0.29 μM	—	Chestnut shell waste extract/TPC		—	—	[94]
		Caffeic acid	1–50 μM	0.14 μM	—			—		
		Rosmarinic acid	1–20 μM	0.09 μM	—			—		
Chronoamperometry (CA)	CuO nano-rice/ GCE	UA	0.83–253 μM	0.83 μM	—	real samples of dopamine injection, human serum and urine samples	pH 7 (PBS)	—	Glucose, Fructose, Galactose	[62]
		DA	0.083–428.8 μM	0.083 μM	—			—		

Table 4.
Evaluation of antioxidant capacity by Amperometric technique.

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
Potentiometry	—	Antioxidant	—	—	—	black and green tea microsuspensions	pH 7.2 (PBS)	—	—	[95]
Potentiometry	GCE	chicoric acid	—	—	—	Echinacea flowers	pH 7.4 (PBS)	—	—	[96]
Potentiometry	POM immobilization on the surface of a glassy carbon electrode	Polyoxometalates (POMs)	—	—	—	—	0.1 M HClO4	—	—	[97]

Table 5.
Evaluation of antioxidant capacity by potentiometric technique.

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
LSV	Ionic liquid-rGO-titania-Nafion-GCE	capsaicin	0.03–10 μM	0.0032 μM	—	Korean hot pepper (Chungyang pepper) solution	pH 1.0 (BRB)	0.75 V	—	[98]
LSV)	gold disk electrode	2-tert-butylphenol (2-TBF)	9.12–80.83 μg cm^{-3}	0.67 μg /L	2.22 μg cm^{-3}	mineral and synthetic oils	0,16 M H_2SO_4	—	—	[99]

Table 6.
Evaluation of antioxidant capacity by linear sweep voltammetry (LSV).

Method	Electrode	Analyte	Linear range	LOD	LOQ	Samples	Optimum pH	Peak Potentials	Interferences	Ref
EI electrochemical index	CPEs (carbon paste electrodes)	TAC	0.105–0.500 μM	40,4 nM	0,105 μM	olive oil samples	pH 7 (PBS)	—	—	[100]
PC peak current			8.02 x 10^{-2} – 0.500 μM	30,5 nM	80,2 nM					
Redox microsensor	Redox measurements	gallic acid	0.2–2 mM	49 μM	148 μM	White wine Serum	pH 5.8	—	—	[73]
			0.1–2 mM	109 μM	331 μM		pH 7			
			0.1–1.5 mM	74 μM	223 μM		pH 8			

Table 7.
Evaluation of antioxidant capacity by other techniques.

3. Conclusion

Electrochemistry is a powerful and versatile analytical technique for the determination of numerous substances such as drugs, pesticides, inorganic, antioxidant-type compounds and electroactive compounds by rapidly possible applications in a lot of fields. Electroanalytical methods besides providing details on quantitative and qualitative of analyte that offer validation parameters such as sensitivity, accuracy and precision, selective and linear working range. Moreover, it is superior to determine the target analyte by electroanalytical methods lack of interferences effect especially in a complex matrix such as biological and food samples contain countless substances. The improvement of simultaneous determination of analytes considerably has been carried out to be applied in biological and environmental systems by the sensitive and selective electrochemistry methods. Because of this, the use of many areas of electrochemistry is widespread.

Nowadays, electrochemical methods, especially voltammetry from medicine to the determination of antioxidants, have made an important place especially in the world of science. Not only analytical chemists but also biology, food engineering and all people who are engaged in food have been used electrochemical methods to determine the antioxidant capacity in plants, tea, beverages, carbonated beverages and solid food samples, etc. Compounds such as ascorbic acid, caffeic, catechin, ascorbic acid, quercetin, gallic acid and coumarin have been widely used as reference standard agents to an evaluation of antioxidant capacity by electrochemical methods have been carried out until today. Due to advances in electronics and computer science have provided significant benefits in terms of electrochemical instrumentation such as accuracy, sensitivity and easy application, the electro-analysis of antioxidant compounds is successfully applied by stripping voltammetric techniques at nM concentration level. The purpose of this review is to show that electroanalytical methods for commonly used antioxidant types may be the best analytical method for the quantitative and qualitative analyte and that they can successfully compete with more conventional methods especially spectrometric methods. Consequently, voltammetric techniques supply that even at low concentrations, the antioxidant capacities of food samples can be determined to be very fast, simple, non-pretreatment and highly sensitive compared to conventional analytical methods. The review presented that the antioxidant capacity of various food samples can be carried out by voltammetric techniques in the estimation in real samples.

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