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Mini Review

Extraction and Electrochemical Analysis of Polyphenols in Plant Samples

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Plant polyphenols are polyphenolic secondary metabolites that widely exists in plants and are mainly found in the skin, root, leaf and fruit. Plant polyphenols are natural antioxidants and are the most powerful free radical scavengers known. Therefore, the extraction and analysis of these polyphenols has attracted considerable attention. In this review, the extraction of plant polyphenols is discussed. Then, we focus on methods for the analysis and determination of plant polyphenols with a specific focus on analysis and detection methods based on electrochemical sensing.

Keywords: Electroanalytical chemistry; Polyphenol, Plant tissue; Analytical method; Analyte

1. INTRODUCTION

Plant polyphenols, also known as tannins, are complex polyphenols isolated from plants. Plant polyphenols are complex secondary metabolites widely distributed in the plant kingdom. People obtain polyphenols from fruits, vegetables, flowers, tea and other plants. Polyphenols have many biological activities, such as causing weight loss, reducing blood pressure, facilitating bacteriostasis, and scavenging free radicals as well as showing anticancer, anti-inflammatory, anti-aging, antitumour, and antioxidation effects, so in-depth studies of plant polyphenols are of great interest [1–9]. In recent years, plant polyphenols from natural sources have been widely used as antioxidants, antimicrobial agents and preservatives due to their significant antioxidant effects [10–17]. They have been used in many fields, such as food, medicine, nutrition and health care [18–28]. The isolation, identification and bacteriostatic properties of polyphenols from different plant tissues have become an active field of research.

Based on their structure, tannins can be divided into hydrolysed tannins and condensed tannins. Plant polyphenols are divided into two types: polygallols and polyflavanols [29–31]. Polygallol species have ester bonds in their molecules. The core of the polyols is composed of ester bonds and phenolic

carboxylic acids. These compounds show poor chemical stability under the action of acid, base or enzymes, making them easy to hydrolyse. Polyflavanols are polymers of flavanols that are chemically stable but condense into water-insoluble substances under strongly acidic conditions [32–37]. The ability to form hydrophobic interactions and multiple hydrogen bonds are important chemical properties of plant polyphenols that can react with alkaloids, polysaccharides and other biomacromolecules. Under the action of multiple ortho-phenol hydroxyl groups and metal ions, polyphenols show complex reactivity, and ortho-phenol hydroxyl groups are easily oxidized, which makes it a good antioxidant. As the public's understanding of plant polyphenols increases, their applications have expanded.

Plant polyphenols are natural pigments, and their effects on food colour are mainly divided into two categories. The polyphenols in potatoes and apples are easily oxidized into quinones under the catalysis of polyphenol oxidase, which makes the fruits turn yellow and brown. On the other hand, the red or ruby colours of wine and black tea are produced by the oxidative fermentation of polyphenols. The content of polyphenols in red wine is relatively high and can reach 1 ~ 3 g/L on average. The polyphenols extracted from green tea, grape seeds and persimmon fruits are used as food additives as antioxidants and preservatives to improve the quality of food. The astringency of polyphenols can prevent the feeding of animals and insects, and this is a self-defence mechanism of plants. High tannin contents adversely affect the taste and flavour of food [38–44]. However, to some extent, a certain amount of astringency in food is necessary to achieve the desired flavour. The tastes and flavours of foods vary from person to person, and some people believe that astringency can promote appetite, especially in many drinks, such as coffee, tea, and wine. Astringency plays an important role in forming unique tastes. Tea polyphenols, a type of polyphenols extracted from tea, are used to preserve cooked foods, as they can inhibit the reproduction of microorganisms and extend the shelf life of food. In the study of chicken nutrition, catechins have antioxidant effects similar to natural vitamin E, and the storage time of frozen chicken can be improved by feeding diets supplemented with catechins [45–51].

In this review, the extraction of plant polyphenols is discussed. Then, we address analysis and determination methods for plant polyphenols, with a special focus on analysis and detection methods based on electrochemical sensing.

2. EXTRACTION OF PLANT POLYPHENOL

The extraction methods for plant polyphenols are generally divided into traditional extraction methods and new extraction methods. The traditional extraction methods include the immersion method, percolation method, decoction method, organic solvent method and reflux extraction method. These methods are often not effective and have disadvantages such as inefficient extraction of the target constituents, high contents of impurities, and poor efficacy. New extraction methods include ultrasound-assisted extraction, microwave-assisted extraction, enzyme-assisted extraction and superfluid extraction. Compared with traditional extraction methods, these new techniques have the advantages of offering high purity, yield and energy efficiency.

The basic principle of the organic solvent method is to separate the target component from the raw material by using the difference in the solubility of the extracted component in various solvents

according to fundamental solubility principles [52–56]. The extraction solvent is mainly selected based on the polarity of the solvent and the target component and the nature of co-existing impurities. Therefore, the selection of the solvent in extraction processes has a significant impact on the efficacy of the extraction. The target should be highly soluble in the selected solvent, while other non-target components should be slightly or insoluble in the extraction solvent [57–62]. Because polyphenols have a polyphenol hydroxyl group, making them somewhat polar, they can be extracted by hydrophilic solvents such as water, ethanol, methanol and acetone. Such solvents can readily solvate and penetrate plant cells. Differences in the raw materials and extraction conditions significantly effect the extraction rate of polyphenols. The reason for these differences may be that the properties and contents of polyphenols as well as the cell wall thickness and permeability differ among various raw materials [63–66]. Although organic solvent extraction requires simple equipment and is operationally simple, the extraction time is long, and the extraction rate is low.

Ultrasonic waves refer to electromagnetic waves with a frequency of approximately 20 ~ 50 kHz. They are a kind of mechanical wave that requires an energy carrier and medium for propagation. Ultrasonic extraction uses mechanical effects to facilitate the destruction of the raw material and may cause the cell tissue to rupture [67–71]. Cavities can be formed by the cavitation effect. The closure of the resonant cavity produces micro-shock waves, which can rupture the plant cell wall throughout the whole organism and increase solute penetration. Heat can be used to increase the dissolution rate of active ingredients to improve extraction rates and shorten extraction times. The breakdown of plant cell walls and whole organisms increases solute penetration. Leandro et al. [72] explored the ultrasonic-assisted extraction of black fruit, and assessed the oxidation resistance of polyphenols from tissues such as the rib gland of rowan; of the parameters that influence the extraction kinetics and extraction yield, including the extraction time and temperature, the composition of the solvent, the material to liquid ratio, the particle size and the use of ultrasonication, they found that the use of ultrasonication had a significant effect on the extraction outcome (the polyphenol yield increased to 85%) [73–77].

Microwave-assisted extraction is mainly based on the thermal effects of microwaves. Because polar substances absorb microwave energy, heat can be produced. The temperature inside the cell increases rapidly, and the pressure inside the cell exceeds the expansion capacity of the cell wall, leading to cell rupture, which makes it easier for the solvent to enter the cell and dissolve and release the target components [78–83]. Microwave-assisted extraction, as a new technology with great potential for development, has the advantages of operational simplicity, low solvent consumption, high efficiency, and short extraction times. In addition, microwave equipment is electrical and does not involve a boiler, which improves efficiency and reduces monetary investment [84–86].

Cellulase, hemicellulase and pectinase can degrade cell walls and intercellular substance. The principle of enzyme-assisted extraction is to select enzymes that can act on plant cells and damage the dense structure of the cell wall, causing local changes such as loosening, expansion and collapse of the cell wall and intercellular structure, facilitating the extraction of the target components [87–92]. Enzymatic extraction can not only improve the extraction rate of active ingredients but also shorten the extraction time. In addition, the enzymatic extraction of plant polyphenols only destroys some of the substances in the cell wall and intercellular matrix and does not damage the stereostructure and biological activity of the target components. Therefore, this technique is beneficial for maintaining the original

characteristics of the target constituents, and enzymatic reaction conditions are generally mild, minimizing the impact on the conformation of the natural products.

Supercritical is used to refer to the state of matter between gas and liquid; the density and solvability of supercritical fluids are close to those of the liquid, and the viscosity is close to that of the liquid [93–101]. The diffusion coefficient is close to that of the gas. Therefore, with a strong permeability similar to gases and a strong solubility similar to liquids, the active ingredients can be extracted from raw materials. Among supercritical materials, supercritical CO_2 is inexpensive, easy to obtain, chemically stable, non-toxic, and pollution-free, and it leaves no residue in the extracts, and thus, it is the most widely used super critical substance. Supercritical fluid extraction has good selectivity, can effectively extract volatile substances, and can effectively avoid the oxidation and decomposition of bioactive substances. The disadvantage of this technology is the high monetary investment required.

3. TRADITIONAL METHODS FOR THE ANALYSIS OF PLANT POLYPHENOLS

UV-vis spectrophotometry is based on the electrons in the outer layer of the molecule absorbing external energy and being promoted to a higher energy level, which is accompanied by transitions in the vibrational energy level and the rotational energy level, resulting in spectral bands. The Lambert-Beer law is the basis of spectrophotometry. Plant polyphenols were determined by spectrophotometry and classified according to their chemical reaction mechanism as follows. (1) Protein precipitation method: the content of polyphenols can be determined by the complex precipitation characteristics of plant polyphenols and proteins. (2) Metal chelation method: the polyphenol content can be quantitively determined based on the properties of the coloured chelates formed by the complexation of the characteristic substituents in plant polyphenols with certain metal ions. (3) Redox method: the polyphenol content is determined based on the reducing ability of the phenolic hydroxyl groups in the plant polyphenols causing the formation of coloured compounds in the presence of oxidants.

The wavelength of near infrared light is approximately 0.75 ~ 2.5 μm. The absorptions of the C-H, O-H and C=O moieties in plant polyphenols, including their combined frequency (corresponding to the simultaneous excitation of two vibrational states in the molecule) and frequency multiplication (transitions corresponding to the vibrational states between one and several energy levels), falls in the near infrared region and produce absorption peaks. Therefore, near infrared spectroscopy is a simple, rapid, low-cost and non-destructive method for polyphenol determination.

Chromatographic methods are used for separation and analysis. Mixtures can be separated by differential migration in a two-phase system based on the differences in adsorption, distribution, molecular size or charge of the components to be measured influencing their relative motion, and the measured components can be analysed qualitatively and quantitatively. One of the most widely used chromatographies is high-performance liquid chromatography (HPLC), which has the advantages of high sensitivity, accuracy, rapidity, simplicity and specificity. In addition, chromatography has certain limitations, as the related methods cannot determine volatile or poorly thermally stable substances.

4. ELECTROCHEMICAL METHOD FOR THE ANALYSIS OF PLANT POLYPHENOLS

Electrochemical detection can be used to analyse the electrochemical properties and charges in solution or other media. These methods are divided into potential analysis, voltammetry and polarography, electrolysis and coulomb analysis. They offer high sensitivity, good selectivity, wide linear ranges and other advantages, and through the study of the electrode process, the mechanism of action of drugs can be explored, making these techniques a popular means of detection. Potential analysis is used to determine the concentration of polyphenols based on the relationship between the electrode potential and concentration. Volt-ampere and polarographic analysis is a unique electrolytic analysis method that uses a working electrode and a reference electrode to form an electrolytic cell, and the electrochemical analysis is conducted according to the current-voltage or other curve recorded in the electrolysis process. Electrolysis and coulomb analysis were the first electrochemical methods described. In recent years, with the development of new electrode materials, the sensitivity of electrochemical detection has been further improved.

Catechins are active phenolic substances extracted from plants such as tea. Catechins are the main functional components in tea, accounting for 12%~24% of the dry weight of tea. After catechins are ingested by the human body, they will be rapidly methylated or glycosylated under the action of enzymes. Methylcatechins are know for their anti-allergy effects and anti-drug resistance effects in tumour cells. The water solubility of glucosylated catechins is significantly higher than that of their parent compound, and glucosylation effectively prevents browning. Acylated catechins have increased antioxidant and anticancer activities due to their increased lipid solubility. A varied electrochemical biosensor has been established for the determination of catechins. Singh and co-workers demonstrated an electrochemical sensor for the determination of catechins based on a gold-nanoparticle–polypyrrole composite that was synthesized in one step [102]. Rahman and co-workers reported a catechin sensor prepared using laccase immobilized on Au nanoparticles encapsulating a dendrimer bound to a conductive polymer [103]. Carbon materials have been widely used for electrode surface modification and enhancing the sensing performances of these systems. For example, Yang and co-workers reported a single-walled carbon nanotube-based electrode modified with cetyltrimethylammonium bromide for the determination of catechin [104]. Vilan et al. [105] reported MnO_2/carbon nanotube/Pt NPs for the sensitive determination of catechin. Veeramani et al. [106] used a lignocellulosic biomass-derived, graphene sheet-like porous activated carbon sensor for the sensitive determination of catechins. Figure 1 shows the scheme of this process.

Gallic acid is widely found in rhubarb, eucalyptus grandis, dogwood and other plants. It is a natural polyphenol and is widely used in food, biology, medicine, the chemical industry and other fields. Abdel-Hamid and Newair reported a polyepinephrine-modified GCE for the adsorptive stripping voltammetric determination of gallic acid [107]. Tashkhourian and Nami-Ana used SiO_2 NP-modified carbon paste electrodes for the electrochemical determination of gallic acid [108]. Their results indicate that SiO_2 NPs significantly improve the current signal of gallic acid due to their high specific surface area and excellent accumulation efficiency.

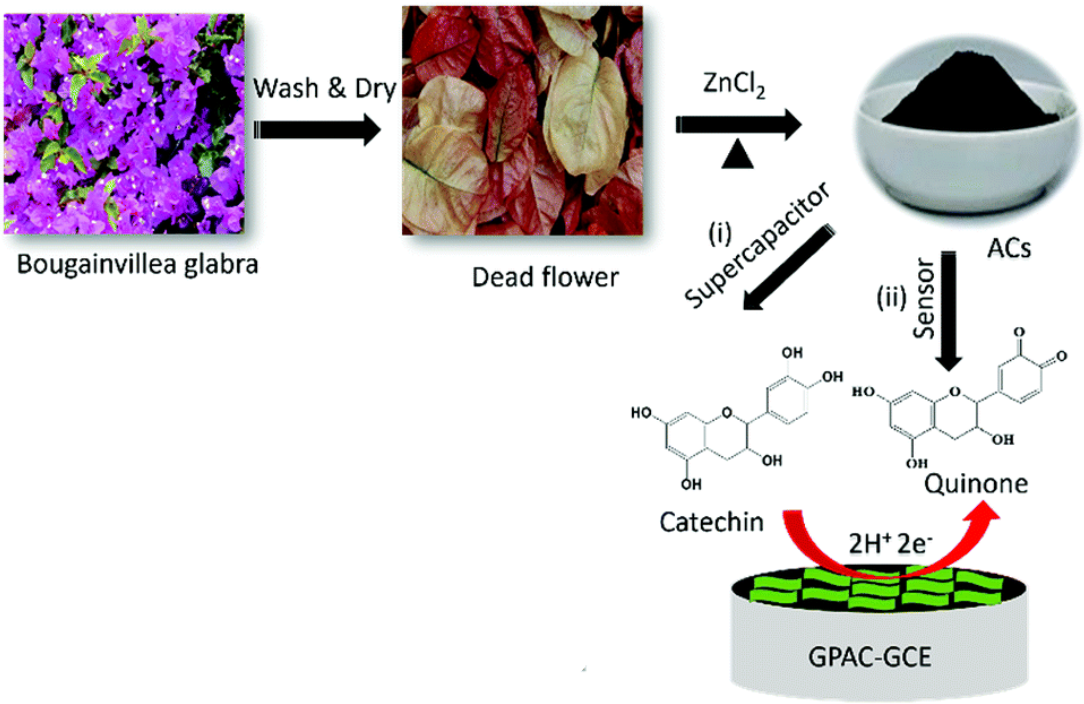

Figure 1. Synthesis of graphene sheet-like activated carbon (GPAC) and its application as an electrode material for sensing catechins [106].

Carbon materials have also been employed for the determination of gallic acid. For example, Ghoreishi et al. [109] reported a multi-walled carbon nanotube-modified carbon paste electrode for gallic acid sensing. The modified electrochemical sensor could detect gallic acid with a linear response from 1 to 33.75 μM. The mechanism of the electrochemical oxidation of gallic acid is shown in Figure 2.

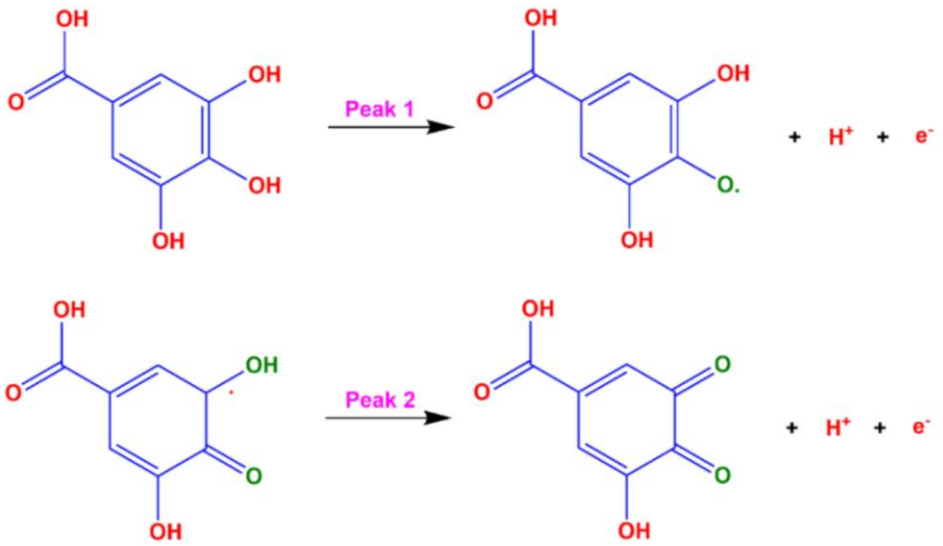

Figure 2. The overall electrochemical oxidation of gallic acid [109].

Caffeic acid, an organic compound, is a type of hydroxycinnamic acid. Because caffeic acid is a key intermediate of lignin, one of the main components of biosynthetic plant biomass and its residues, it is widely found in various plants. Trabelsi et al. [110] reported the electrochemical behaviour of caffeic acid in 2004. Since then, many studies have focused on the development of electrochemical sensors for caffeic acid detection. Moghaddam et al. [111] further reported the electrochemical behaviour of caffeic acid with a single-walled carbon nanotube. Leite et al. [112] fabricated molecularly imprinted siloxanes for the sensitive determination of caffeic acid. Manikandan and co-workers demonstrated a fluorine-doped graphene oxide for caffeic acid sensing [113]. Figure 3 shows the DPV responses of fluorine-doped graphene oxide-modified GCEs in the detection of caffeic acid at concentrations ranging from 0.5 to 100.0 μM.

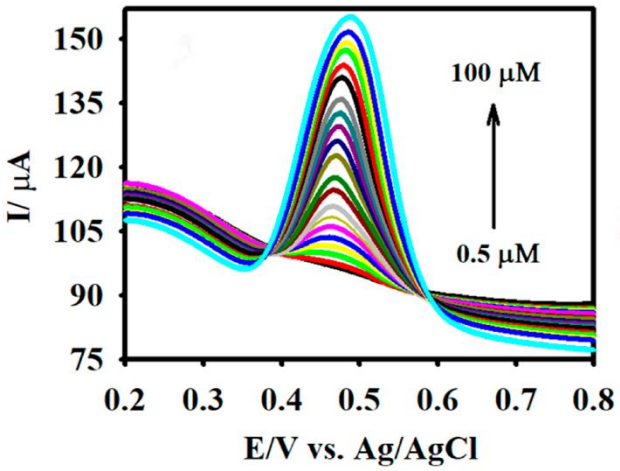

Figure 3. The DPV responses of fluorine-doped graphene oxide-modified GCEs for the detection of caffeic acid at concentrations ranging from 0.5 to 100.0 μM [113].

Kaempferol, a natural flavonoid, is a phytogenic substance found in tea, broccoli, lark finch, witch hazel, grapefruit, Brussels sprouts, apples and other plants. Recently, Dar and co-workers reported the electrochemical behaviour of kaempferol with multi-walled carbon nanotube-modified carbon paste electrodes. We believe that in the future, more scholars will focus on the electrochemical detection of kaempferol.

Rutin is a flavonoid compound that is used in many countries to provide vascular protection and as a multivitamin and herbal remedy. He and co-workers reported the electrochemical determination of rutin based on β-cyclodextrin-incorporated carbon nanotube-modified electrodes [114]. Xing and co-workers reported a electrochemical sensor using palladium phthalocyanine-MWCNTs-Nafion nanocomposite for the sensitive detection of rutin [115]. Under the optimized conditions, the proposed electrochemical sensor could linearly detect rutin from 0.1 to 51 μM with a low detection limit of 75 nM. Rutin can also be detected using a graphene oxide and multi-walled carbon nanotube nanocomposite [116]. Figure 4 shows the DPV sensing performance of a graphene oxide and multi-walled carbon

nanotube nanocomposite towards different concentrations of rutin. Under the optimum conditions, the electrochemical sensor exhibited two linear ranges: 0.08~10.0 μM and 10.0~80.0 μM.

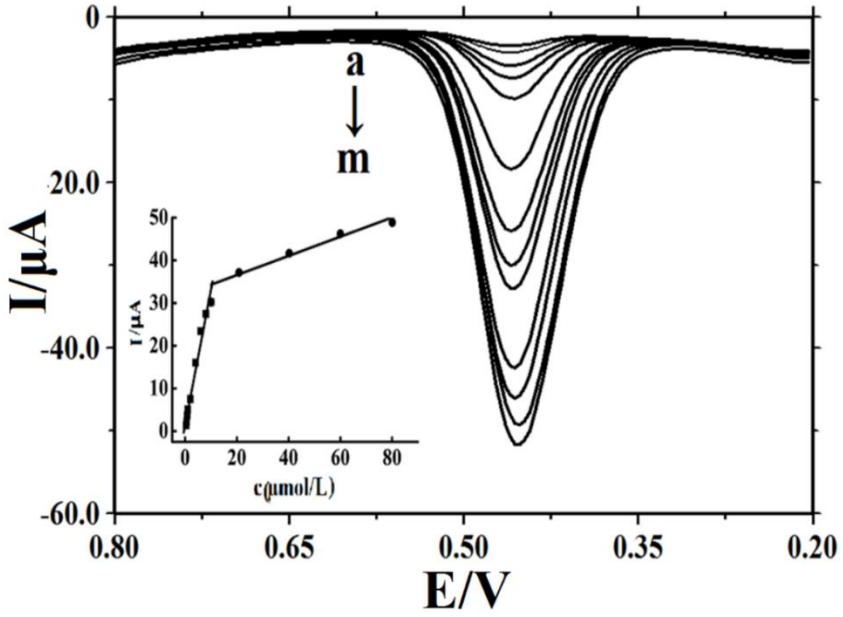

Figure 4. DPV of various concentrations of rutin with a graphene oxide and multi-walled carbon nanotube nanocomposite [116].

Table 1. Summary of recent development of electrochemical method for polyphenols detection.

Analyte	Method	Detection range	Reference
Epigallocatechin	SWV	0.1 μM to 1 μM	[117]
Catechin	DPV	1 nM to 10 nM	[102]
Catechin	DPV	0.1−10 and 0.05 ± 0.003 μM	[103]
Catechin	CV	0.3268 μM to 0.1591 mM	[118]
Catechin	CV	0.372 nM to 2.38 nM	[104]
Catechin	SWV	-	[119]
Catechin	CV	10 μM to 60 μM	[120]
Catechin	SWV	-	[121]
Catechin	CV	-	[122]
Catechin	CV	4–368 μM	[106]
Catechin	SWV	0.25 μM to 50 μM	[123]
Gallic acid	DPV	1.0 to 20.0 μM	[107]
Gallic acid	CV	80 nM to 0.1 mM	[108]
Gallic acid	DPV	1 μM to 33.75 μM	[109]
Gallic acid	CV	1 μM to 100 μM	[124]
Gallic acid	LSV	0.1 to 10 mg/L	[125]
Gallic acid	CV	-	[126]
Gallic acid	DPV	0.60 μM to 8.68 μM	[127]
Gallic acid	DPV	6.24 nM to 477.68 nM	[128]

Caffeic acid	DPV	0.5 μM to 60 μM	[112]
Caffeic acid	CV	0.1 μM to 50 μM	[129]
Caffeic acid	DPV	5.0 nM to 450.55 μM	[130]
Caffeic acid	DPV	0.03 μM to 938.97 μM	[131]
Caffeic acid	DPV	-	[132]
Caffeic acid	CV	0.2 μM to 2100 μM	[133]
Caffeic acid	DPV	5 nM to 50 μM	[134]
Caffeic acid	DPV	19 μM to 1869 μM	[135]
Caffeic acid	DPV	0.055 μM to 2455 μM	[136]
Caffeic acid	DPV	0.01 μM to 608 μM	[137]
Caffeic acid	DPV	0.5 μM to 100.0 μM	[113]
Kaempferol	DPV	6.72 nM to 40.34 nM	[138]
Rutin	DPV	0.4 μM to 1 mM	[114]
Rutin	CV	0.5 μM to 0.1 μM	[139]
Rutin	DPV	0.1 μM to 51 μM	[115]
Rutin	DPV	10 nM to 0.5 mM	[140]
Rutin	DPV	0.1 μM to 0.8 mM	[141]
Rutin	DPV	72 nM to 6 μM	[142]
Rutin	DPV	4 nM to 60 μM	[143]

4. CONCLUSION

Polyphenols are renewable green resources and important secondary metabolites in plants, and they have a variety of biological activities and play an important role in human health. Their development and application have great potential, and they have become the focus of a substantial amount of research. In this review, we first describe the extraction of polyphenols from plants. Then, we describe in detail electrochemical analysis and detection methods for plant polyphenols. Flavanols, catechins, gallic acids, caffeic acids, kaempferol and rutin are the most common polyphenols in plants. We reviewed the development of electrochemical methods for sensing these substances in detail.

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