Electrochemical strategies for determination of *tert*-butyl hydroquinone (TBHQ) in food samples

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Abstract

Tert-butyl hydroquinone (TBHQ) is a member of the synthetic phenolic antioxidant family that prevents the formation of free radicals and prevents radicals from damaging cells by trapping them. In addition, TBHQ is widely preferred as an additive in foods and vegetable oils because of its low cost and high chemical stability. TBHQ is not only a food preservative but is also frequently used as a stabilizer to prevent auto-polymerization in cosmetics, biodiesel, pharmaceuticals, coating products, and different application areas. TBHQ has been shown to cause diseases, such as DNA damage, carcinogenesis, and cell apoptosis, when administered at high doses. Excessive consumption of TBHQ causes adverse effects, such as stomach tumors, liver damage, and underdevelopment of the reproductive system. Different analytical methods have been used to detect TBHQ in food samples. The most important of these methods are traditional analytical methods such as chromatographic and spectrophotometric methods. However, these methods have basic shortcomings such as high analysis costs, long pre-processing, expensive equipment, need for many organic solvents, requiring expertise, and long detection times. In recent years, electrochemical sensors have attracted attention in the scientific world owing to their high sensitivity, fast analysis time, portability, low cost, and convenience of miniaturization. This review discusses electrochemical studies performed to date for the determination of TBHQ in food samples. The methods used in these studies have been evaluated in a wide range of aspects, such as the electrode, working range, detection limits, and analytical applications.

Introduction

Antioxidants have a phenolic function in their structure, preventing the formation of free radicals and preventing radicals from damaging the cell by trapping them [1, 2]. This substance is necessary for human health and is abundant in foods, especially citrus fruits such as lemons, oranges, and tangerines. Antioxidants also play a major role in eliminating oxidative stress, which plays a critical role in the etiology of some diseases. Therefore, these antioxidants, which are necessary for raising healthy generations, are abundantly available or used in foods, both naturally and synthetically. Synthetic and natural antioxidants have attracted significant attention. Promotes the use of synthetic antioxidants as food additives for the nutrition of healthy individuals.

Tert-butyl hydroquinone (TBHQ) is a member of the synthetic phenolic antioxidant (SPA) family [3]. Similar to SPAs, TBHQ is preferred as an additive in foods, oils, and other substances because of its low cost and high chemical

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stability [4]. This is another reason why TBHQ is preferred, because it provides long-term protection [5]. TBHQ produces active hydrogen that combines with free radicals released by the oxidation process, providing long-term storage and preservation of foods. TBHQ, known as a food preservative, is also frequently used in cosmetics, biodiesel, pharmaceuticals, coating products, and in different application areas as a stabilizer to prevent autopolymerization [6]. TBHQ is also 6–8 times more effective than other synthetic phenolic antioxidants such as butyl hydroxyanisole (BHA), 2,6-di-tert-butyl-4-methylphenol and propyl gallate (PG) [3]. However, synthetic phenolic antioxidants have also been shown to have adverse effects on human health [3]. High doses of TBHQ as 0.7 mg/kg have been shown to cause diseases such as DNA damage [7], carcinogenesis [8], and apoptosis [9, 10]. In addition, excessive consumption of TBHQ has been found to cause adverse effects, such as gastric tumors, liver damage [11, 12], and reproductive system underdevelopment [4]. In addition, negative effects on human health, such as excessive use of SPAs and carcinogenic, estrogenic, and genotoxic effects, have been observed [4, 12–16]. . It is well known that the oxidative product of TBHQ, tert-butylbenzoquinone (TBBQ), is also cytotoxic [17]. Therefore, a limitation has been imposed on the use of TBHQ, and its use has also been banned in some countries [18]. According to the World Health Organization (WHO) and US Food and Drug Administration (FDA), the daily TBHQ consumption amount was determined as 0-0.2 mg/kg. In China, Australia, Brazil, and other countries, the maximum allowable use of TBHQ in food is limited to 200 mg/kg [3, 19, 20]. The use of TBHQ in foods is prohibited in Japan, the European Union, and other countries [18]. Since TBHQ directly affects human health, TBHQ determination is of great importance and requires routine analysis. Fast, reliable, selective, and sensitive TBHQ analyses are required for quality control procedures in food.

To date, different analytical methods have been used to detect TBHQ in food samples. The beginning of these methods is conventional analytical methods such as high-performance liquid chromatography (HPLC) [21], gas chromatography (GC) [22], and spectrophotometry [23]. However, HPLC, GC, and spectrophotometry methods have shortcomings such as high analysis costs, long pre-processing, expensive equipment, need for too many organic solvents, require expertise, and long detection times. In addition, they are not suitable for green chemistry because they require many organic solvents and generate a large amount of waste after analysis. Scientists are seeking alternative methods to eliminate these deficiencies in the analysis of vital substances. Especially in recent years, electrochemical sensors have attracted attention in the scientific world owing to their high sensitivity, fast analysis times, portability, low cost, and miniaturization convenience. Therefore, they are widely used for the detection of numerous analytes in food, pharmaceutical, and environmental samples. Moreover, hybrid probes combined with nanosensors and new materials developed in recent years have contributed significantly to this process. It has been applied because of its excellent electrochemical properties in the determination of both biologically important and controlled substances, such as pharmaceuticals, food additives, pesticides, metals, and nucleic acids.

Since the hydroxyl (-OH) functional groups in the TBHQ structure can be easily oxidized to quinones, scientists have benefited from the oxidase electrode reaction in real samples, such as food and biodiesel [21] (Fig. 1). Because this situation is caused by phenolic groups, the total amount of antioxidants in food and vegetable oil samples was determined according to TBHQ. Contrary to traditional antioxidant
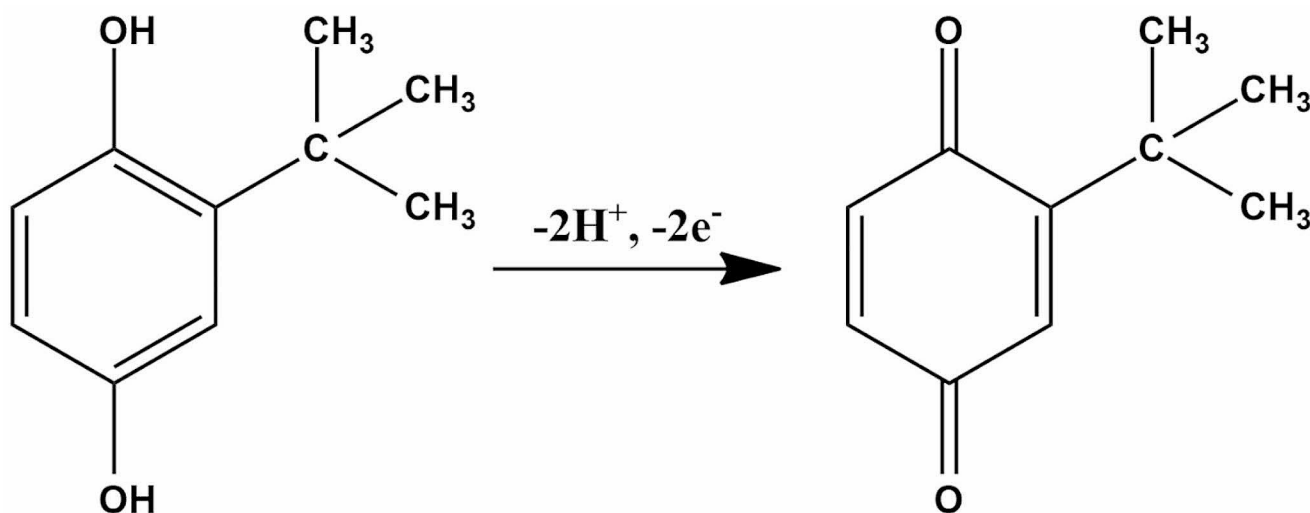

Fig. 1 The oxidation mechanism of TBHQ

determination methods, faster, more sensitive, and reliable determination of total antioxidant amount can be performed with TBHQ. This makes the determination of TBHQ in food samples important and paves the way for further research. In addition to electrochemical studies, the development of a sensor detector, which can be combined with advanced analytical instruments such as HPLC, and the qualitative and quantitative determination of TBHQ have been carried out [21]. Combined analyzer systems that combine HPLC for the determination of the synthetic antioxidant TBHQ in food samples are among the promising innovations for the future (Fig. 1).

In recent years, numerous substances have been quickly, simply, and selectively analyzed using electrochemical methods. The most important emphasis here is that electrochemical methods are fast, easy to miniaturize, and provide on-site analysis opportunities. Therefore, these methods have attracted considerable attention from scientists. Moreover, nanomaterials play an important role in the determination of many different analytes, from drugs to inorganic substances. Among these, the determination of TBHQ, a

synthetic antioxidant, has been carried out with highly predictive success using electrochemical methods in different matrix environments. The most important methods are square wave voltammetry (SWV), differential pulse voltammetry (DPV), cyclic voltammetry (CV), and amperometry techniques (Fig. 2). TBHQ determination in food samples was successfully performed by taking advantage of its electrochemical superiority. Nanosensors combined with other analytical devices were manufactured. Therefore, faster, more selective, and sensitive analytical techniques have been developed for the determination of TBHQ. Moreover, in these studies, more sensitive, selective, and micro-sized sensors have been used with nanomaterials developed in recent years. Many different nanomaterials have been preferred for the determination of TBHQ, a synthetic phenolic antioxidant, in food samples. among these, carbon nanosensors exhibit unique properties. These carbon electrodes include carbon paste electrodes (CPE), carbon nanotubes (CNTs), graphite rod electrodes (GRE), glassy carbon electrodes (GCE), single and multi-walled carbon nanotubes (SWCNTs and MWCNTs), carbon black paste electrodes

Fig. 2 Electrochemical methods in the TBHQ determination
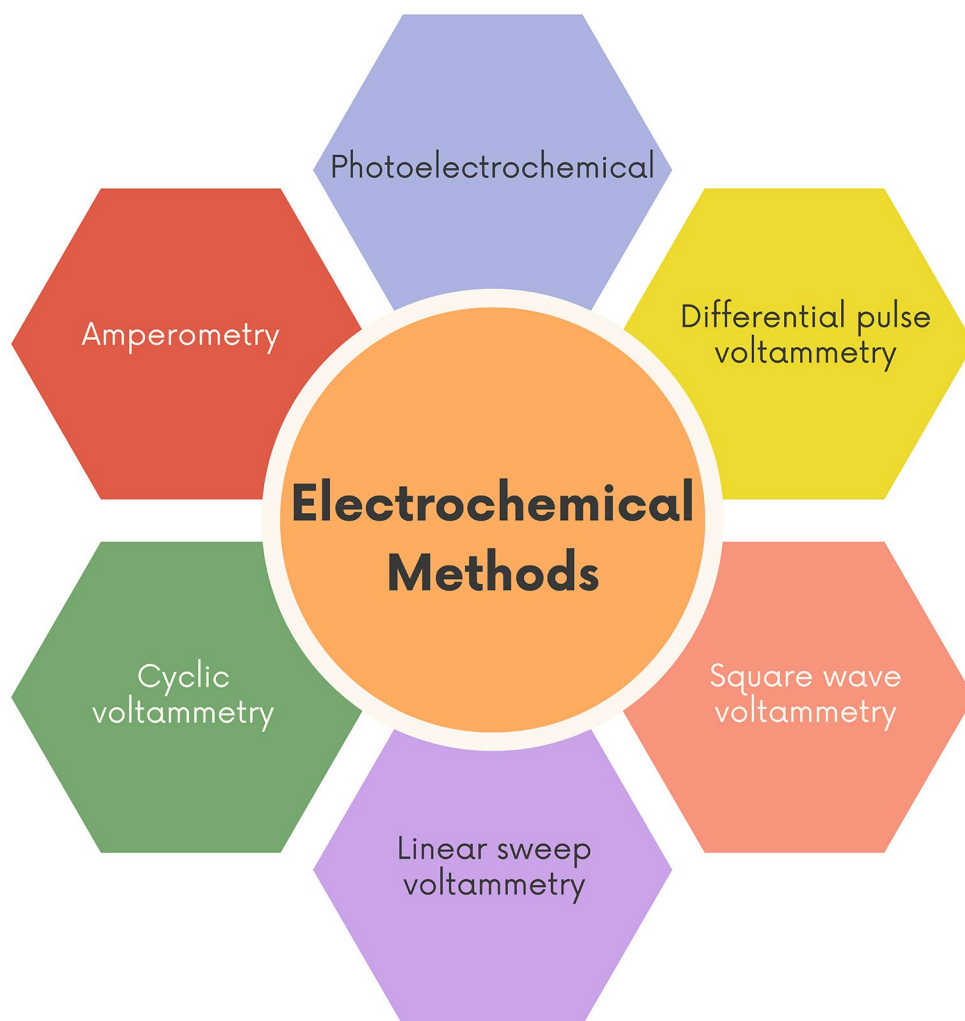
(CBPE), reduced graphene oxide (rGO), carbon fiber micro-electrodes (CFME), and screen-printed carbon electrodes (SPCE). Nanocomposite sensors have also been constructed using polymers, metal oxide nanoparticles, and amino acid monomers for TBHQ determination. Taking all these into consideration, in this review, important validation parameters of electrochemical methods for the determination of TBHQ in food samples in recent years, such as the working range, detection limits, sensor diversity, and analytical applications, have been criticized.

The role of electrochemistry in TBHQ determination

Electrochemistry is a branch of science that studies the changes occurring in the analyte as a result of the interaction of electrical factors, such as current, potential, resistance, and electron charge. This electrical change process plays an important role in the qualitative and quantitative determination of a substance. In addition, very rapid electrochemical processes enable sensitive analysis of the analyte within seconds. In addition, miniaturized devices enable on-site analysis of analytes owing to the portability of the integrated sensors. Although its electrochemical foundations were established in the early 19th century, sensor studies have accelerated with the discovery of carbonaceous materials as an analytical method since the 1980s. Electrochemical studies using nanomaterials that exhibit extraordinary properties have gained immense attention for sensor development. Owing to these unique properties, electrochemical methods are widely used for the determination of numerous substances such as TBHQ (Fig. 2).

DP voltammetry

Differential pulse voltammetry (DPV) is a pulse technique. The basic working principle is that in DPV, increasing potentials are applied in the form of narrow amplitudes and short pulses, similar to steps, depending on time. The Faradaic current occurring on the indicator electrode surface is measured before the application of the pulse and near the end of the pulse, and calculated by taking the difference. For this reason, the analysis time of DPV is slightly longer than of, CV, SWV, and amperometry. However, its biggest advantage over other electrochemical methods is its low residual (capacitive) current, resulting in high sensitivity. DPV and its stripping module, DPSV, provide high accuracy and precision in the determination of analytes at nanomolar (nM) levels in a very short analysis time. Moreover, owing to high selectivity and excellent reproducibility

of DPV, simultaneous determination of numerous analytes has been achieved. Owing to these all the above-mentioned unique properties, it is not surprising that TBHQ is the most commonly used DPV for the determination of food samples.

Among electrochemical methods, DPV is by far the most commonly used method for TBHQ determination. The most important reason for this is that the DPV is a sensitive technique. DPV, which exhibits high selectivity, especially in complex matrix environments, such as food, has contributed greatly to its preference. Considering the studies conducted with DPV, most hybrid electrodes were developed, and only three studies performed TBHQ determination with CBPE, activated GCE, and platinum electrode (Pt E) [19, 24, 25]. In the development of hybrid electrodes a wide range of nanomaterials have been used in the development of hybrid electrodes, including carbon materials, polymers, metal oxide nanoparticles, bimetallic materials, and dyestuffs. These nanomaterials were coated on the surfaces of the main electrodes, such as CFME, GCE, graphite paste electrode (GPE), SPCE, and PtE with different modification processes for the determination of TBHQ in food samples. It is understood that TBHQ was easily determined in μM using DPV on the recommended sensors. Moreover, sufficient studies have been conducted for the determination of TBHQ at the nanomolar (nM) level. In fact, an extremely sensitive DPV technique with a limit of detection (LOD) of 148 pM was developed with the AgNP/POM/rGO/GCE electrode. Additionally, other studies have demonstrated that TBHQ can be detected at a concentration of 1 nM using ZnCuMg TMO/β-CD-CB/SPCE and Co_3O_4 NRs/FCB/SPCE, 1.8 nM with ADC/GCE, 4 nM with TiO_2/NC/GCE, 5 nM with MIP/GNP/MWCNT/GCE, and 9 nM with PVP–CTAB/Au–PVP–Gr/GCE as hybrid sensors. Indeed, almost all DPV studies developed for the detection of TBHQ have a working range and sensitivity that can easily compete with other traditional analytical methods. TBHQ was determined using DPV with extremely high accuracy and precision, especially for vegetable oils such as arowana oil, blend oil, canola oil, colza oil, corn oil, cumin oil, edible oil, flaxseed oil, mizone oil, olive oil, peanut oil, rapeseed oil, sesame oil, soybean oil, sunflower seed oil, walnut oil, and beverages such as apple juice, ice red tea, and orange juice. They also determined TBHQ in different food samples, such as dehydrated soup, beef tallow, biscuits, flour samples, fried chips, mayonnaise, margarine, and roasted nuts on the nanosensors. Moreover, in studies carried out with the DPV technique, the surface morphology and characteristic structural features of the proposed modified nanosensors were examined by using different methods such as atomic force microscopy (AFM), CV, energy-dispersive ray spectroscopy (EDX), electrochemical impedance spectroscopy (EIS), field emission scanning electron microscope (FE-SEM), Fourier-transform infrared

(FTIR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), thermogravimetric analyzer (TGA), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) (Fig. 3). The studies summarized in Table 1 for the determination of TBHQ in food samples using the DPV technique demonstrated outstanding analytical performance.

In the most sensitive study conducted with DPV for the determination of TBHQ by Qin et al., a hybrid sensor containing reduced graphene oxide (rGO) based silver nanoparticles (AgNPs) and $H_3PW_{12}O_{40}$ (POM) treated with a GCE surface was developed [26]. The surface morphology of the developed MIP/AgNP/POM/rGO/GCE nanosensor was elucidated by EIS, XRD, and XPS. Moreover, they found linear operating range on the recommended MIP/AgNPs/POM/rGO/GCE nanosensor to be 0.05–1.5 nM under optimum conditions with DPV. For TBHQ determination, the LOD value was calculated as 14.8 pM. They compared it with other studies on DPV for TBHQ detection and proved that they have constructed the most sensitive nanosensor thus far. Finally, they applied the nanosensor analytically to food matrices such as grape juice and wine and performed predictive analysis with high TBHQ recovery and low relative standard deviation (RSD). As a result, in determining TBHQ, this study, carried out by DPV on the MIP/AgNPs/POM/rGO/GCE, is not only the most sensitive electrochemical method, but also has a detection limit that can easily compete with other classical analytical methods.

In another sensitive study on TBHO analysis, Sebastian et al. constructed a composite indicator electrode by coating

carbon black (CB), β-cyclodextrin (β-CD), and ternary metal oxide (TMO, such as ZnCuMg) on the surface of a screen printed carbon electrode (SPCE) [27] (Fig. 4). They manufactured the ZnCuMg nanomaterial used to make this indicator using hydrothermal process. The surface morphology and chemical structure of the nanosensor were investigated by EIS, EDS, FTIR, Raman spectroscopy, SEM, and XRD. They found that the modified electrode (ZnCuMg TMO/β-CD-CB/SPCE) increased the anodic signal of TBHQ by approximately 15 times compared to that of the bare SPCE. Moreover, the nanosensor exhibited electro-catalytic properties by shifting the TBHQ oxidation potential to a less positive region. They also calculated the active electrode surface in 0.05 M potassium ferricyanide prepared by 0.1 M KCl solution using the Randle-Sevcik equation. The nanosensor recommended for TBHO analysis has an exceptionally wide operating range of 0.031–12.56 μM and a detection limit of 1 nM by providing an excellent faradaic current. They examined the selectivity of DPV and nanosensor in TBHQ determination in the presence of synthetic antioxidants, some organics, various cations, and anions. Finally, using DPV and nanosensor, they successfully determined TBHQ in food samples such as canola oil, flaxseed oil, and sesame oil with high recovery and low relative error. As a result, TBHQ determination by DPV on the ZnCuMg TMO/β-CD-CB/SPCE nanosensor has a level of accuracy, precision, reproducibility, and detection limit that can compete with those of other analytical methods. This shows that the DPV electrochemical technique can be used very easily in routine TBHQ analyses.

In their study in 2022, Inoque et al. developed a 3D polylactic acid (PLA) filament sensor filled with conductive carbon black (CB) for the determination of butyl hydroxyanisole (BHA) and TBHQ synthetic antioxidants used in biofuels (Fig. 5) [28]. The new nanosensor developed showed a catalytic effect and shifted the electrochemical oxidation of TBHQ to a lower potential of 0.2 V. This caused a clearer separation of the TBHQ and BHA anodic peaks and allowed simultaneous determination of both substances in biofuels by DPV. Linear response in the range of 0.5 to 175 μM was obtained by simultaneous determination of TBHQ and BHA on the 3D printed CB/PLA indicator electrode under optimum conditions. In addition, the detetion and quantity limits for both substances were determined as 0.15 μM and 0.5 μM, respectively. They then investigated the effect of some cations on the oxidation peaks of both synthetic antioxidants and found that no interfering species interfered with the determination of TBHQ and BHA. Finally, they carried out the analytical application of soybean biodiesel and commercial biodiesel samples. TBHQ and BHA were determined with high recovery and low relative error. As a result, they developed a fast, sensitive, and selective method with 3D-printed CB/PLA electrodes TBHQ and BHA in food samples.
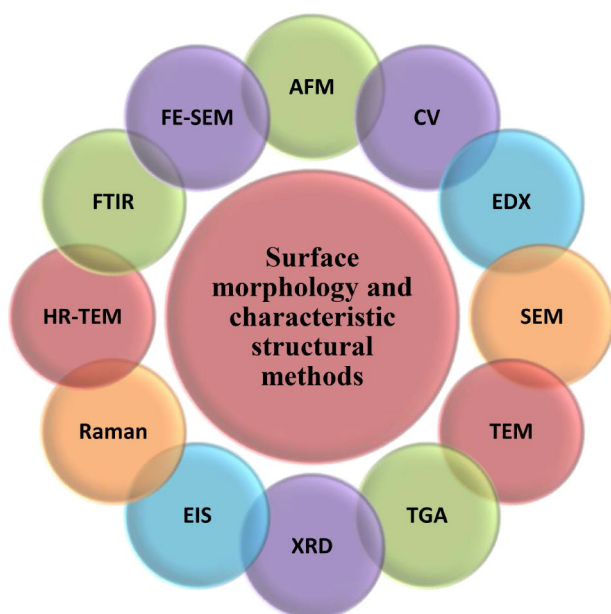

Fig. 3 Analytical methods used to elucidate nanosensor surface morphologies and structures in electrochemical studies

Table 1 The recommended DPV analytical performance for TBHQ determination

Electrode	Method	Working range (μM)	LOD (μM)	LOQ (μM)	Analytical application	Ref
CBPE in the presence of cationic surfactant CPB	DPV	0.27–45.0	0.08	0.27	Mayonnaise, margarine and biodiesel	[24]
MIP/ZC/GCE	DPV	1.0–75.0	0.42	-	Edible oil	[29]
ZnCuMg TMO/β-CD-CB/SPCE	DPV	0.031–12.56	0.001	-	Canola oil, flaxseed oil, sesame oil	[27]
Au–SnO$_2$/GNs-SWCNTs/GCE	DPV	0.05–230.0	0.058	-	Ice red tea, mizone oil and arowana oil	[30]
Graphene/ choline/GCE	DPV	0.40–120.0	0.14	-	Soybean oil, peanut oil, rapeseed oil, and corn oil	[31]
MnO$_2$/ERGO/GCE	DPV	1.0–300.0	0.8	-	Peanut oil and blend oil	[32]
Au$_3$Pt$_3$/GCE Bimetallic	DPV	0.35–625.0	0.075	-	Canola oil, and soybean oil	[33]
ZnO/ZnNi$_2$O$_4$ @porous carbon@COF$_{TM}$/GCE	DPV	0.04785-130.0	0.016	-	-	[34]
Co$_3$O$_4$ NRs/FCB/ SPCE	DPV	0.12–62.2	0.001	-	Beef tallow, peanut oil, and lake water	[35]
Activated GCE	MLLE-DPV	30- 1203.0	10.8	-	Aftab, bahar, and mahya edible oils	[19]
NiPcTs/PPy/PtE	DPV	20–220.0	7.4	25	Mushroom cream	[36]
MIP-MWCNT/GCE	DPV	2.27–68.07	0.85	-	Soybean oil, margarine, mayonnaise and biodiesel	[37]
MIP/AgNPs/POM/rGO/GCE	DPV	0.00005–0.0015	0.0000148	-	Soybean oil, blend oil and beef tallow	[26]
ADC/GCE	DPV	0.4–400.0	0.0018	-	Fried chips, biscuits, and roasted nuts	[38]
PtE	DPV	30–100.0	-	-	-	[25]
P3MT/CFME	DPV	10–700.0	0.25	0.83	Dehydrated soup samples	[39]
CuTSPc/rGO/GCE	DPV	0.1–500.0	0.045	-	Biodiesel samples	[40]
CB/PLA 3D printed Electrode	DPV	0.5–175.0	0.15	0.5	Soybean biodiesel and commercial biodiesel sample	[28]
PVP–CTAB/Au–PVP–Gr/GCE	DPV	0.02–100.0	0.009	-	Flour samples	[41]
Eosin Y/GCE	DPV	0.45–31.77	0.045	-	Corn oil, sesame oil, blend oil, sunflower seed oil, and rapeseed oil	[42]
TiO$_2$/NC/GCE	DPV	0.05–100.0	0.004	-	Soybean oil and colza oil	[4]
MOF/Co/NCNTs/GCE	DPV	0.05–80.0	0.01	-	Soybean oil and sesame oil	[43]
MIP/GNP/MWCNT/GCE	DPV	0.1–1000.0	0.005	-	Black cumin oil, walnut oil and olive oil	[44]
Co NC/CNT/MB/GCE	DPV	0.1–100.0	0.054	-	Soybean oil and peanut oil	[45]
SWCNTs/GPE	DPV	0.05–390.0	0.01	-	Soybean oil, orange juice, and apple juice	[46]

SW voltammetry

Voltammetry methods consist of techniques that measure the non-spontaneous charge transfer processes at the working electrode interface of the substance and the current and voltage that occur depending on the potential difference applied in the supporting electrolyte cell [47]. The purpose of voltammetric techniques is to detect the anodic or cathodic reactions of electroactive analytes and determine them quantitatively in real samples. Additionally, these techniques provide critical information about some electrochemical behaviors that may not be available in other analytical studies, such as charge transfer, thermodynamics, mechanism elucidation, and kinetics of electroactive substances [47].
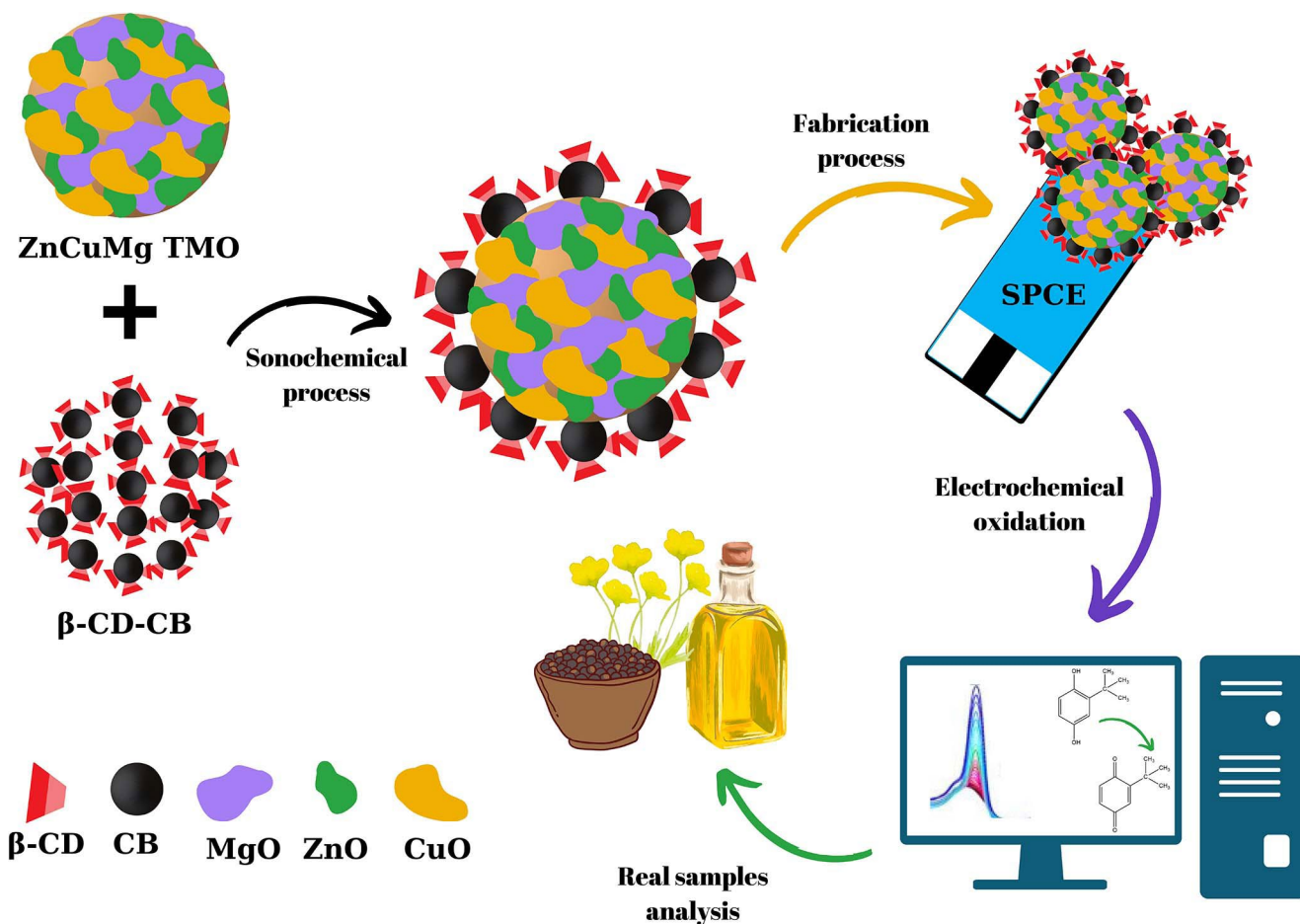
Fig. 4 General fabrication scheme of ZnCuMg TMO/β-CD-CB/SPCE hybrid electrode in DPV study for the determination of TBHQ [27]
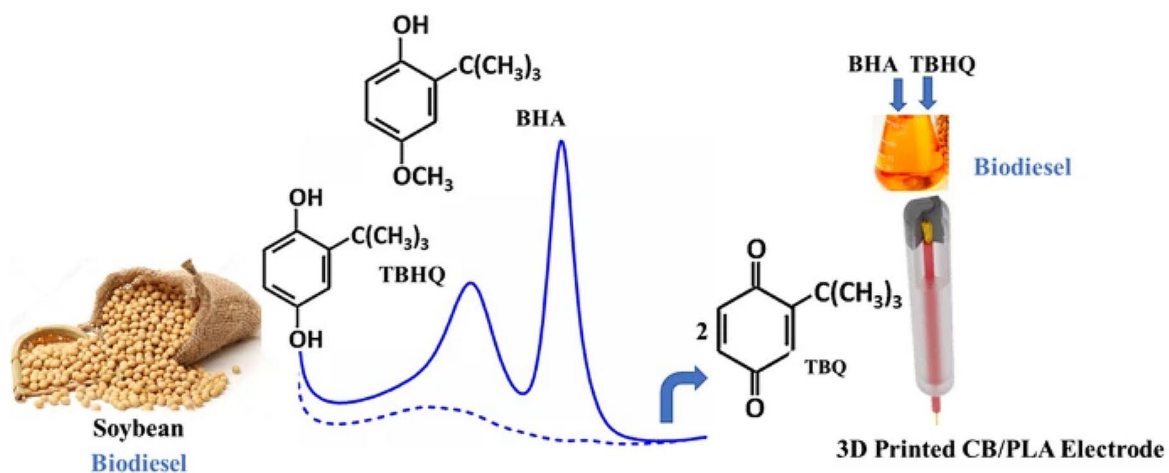

Fig. 5 General fabrication scheme of 3D printed CB/PLA electrode for the determination of TBHQ by DPV. Reproduction with permission from [28]

Square wave voltammetry, the potential increase by pulse is applied in successive steps and the current occurring at the electrode interface is measured at the end of each step. Thus, the current and voltage occurring in seconds is determined, and both the sensitivity of the voltammetric measurement and the quality of the voltammogram are significantly increased. SWV is the most sensitive electrochemical method. In addition, because the accumulation of substances can be applied to this technique, it allows the determination of even trace amounts of analytes. Therefore, SWV and square wave stripping voltammetry (SWSV) techniques are the most preferred in the determination of innumerable substances.

SWS and SWSV are among the preferred techniques in the determination of TBHQ for food samples. Carbon-based nanosensors have been extensively used in studies conducted usingSWV or SWSV. While carbon indicator electrodes are sometimes used alone, they are sometimes preferred in hybrid treatment with nanomaterials such as nanoparticles, ionic liquids, and biochar (Table 2). The main purpose is to improve the catalytic properties of the main electrodes, such as CPE and GCE, and to increase the sensitivity of THBQ determination. The most sensitive studies developed for TBHQ determination were carried out with extremely complex indicator electrodes containing metal oxide nanoparticles, carbon nanomaterials, ionic liquids (Fe_3O_4-SWCNTs/1H3MITFB/CPE) [48], and gold nanoparticles decorated on tungsten carbide AuNP-WC treated with GCE at nanomolar levels [49]. Other electrochemical studies also have predictive detection limits, which should not be underestimated. In fact, all SWV and SWSV techniques developed for TBHQ determination have sensitivity and selectivity that compete with other traditional analytical methods. Moreover, TBHQ determination in mayonnaise, margarine, vegetable oils, biodiesel, red wine, juices and drinking water was successfully carried out with high accuracy and precision and low relative error by SWV and square wave anodic stripping voltammetry (SWASV). In addition, the surface morphology and structural characteristics of

the developed electrodes were illuminated using methods such as Brunauer–Emmett–Teller (BET), EIS, EDX, FE-SEM, SEM, TEM, XPS, and XRD [49–51] in SWV determination.

In a study carried out by Ezhil Vilian et al. published in 2021, they produced a highly successful new-generation composited electrode coated with gold nanoparticles decorated with tungsten carbide (AuNP-WC) on the GCE surface for sensitive determination of TBHQ [49] (Fig. 6). First, the AuNP-WC hybrid material was developed by adhering AuNPs onto WC using an ultrasonic technique. This composite material was then dipped in ethanol to obtain a homogeneous solution of 2.0 g/L was obtained. Then, this AuNP-WC was modified in diperse solution in a volume of 5.0 µL onto the clean and polished GCE surface using the drop-dry technique. The sensitivity of the developed composite electrodes in the determination of TBHQ was examined, and it was determined that the most sensitive sensor was AuNP-WC/GCE by SWV. Moreover, the surface morphology and structure of the developed electrode were elucidated by EDX, XPS, SEM, TEM, XRD, BET, and EIS methods. The electrochemical behavior, kinetic model, number of electrons transferred to TBHQ and pH effect were investigated by CV on AuNP-WC/GCE. They examined the parameters affecting the SWV current and potential, and created a calibration chart. They obtained the dynamic working range for TBHQ determination with SWV as 0.5–75.0 nM and calculated the LOD value as 0.2 nM on the hybrid electrode. They successfully applied their proposed hybrid electrode and electrochemical strategy to food samples, such as soybean oil, blended oil, and red wine, to study their accuracy and efficiency. The determination of TBHQ in real samples was predictive of a high recovery (88–99%) and low relative standard deviation (RSD%, 1.49–3.22%). As a result, this was the most sensitive study conducted with SWV. In particular, the fact that the LOD nM is more sensitive is preliminary evidence that this electrochemical method can compete with other analytical methods.

Table 2 The recommended SWV analytical performance for TBHQ determination

Electrode	Method	Working range (µM)	LOD (µM)	LOQ (µM)	Analytical application	Ref
CBPE in the presence of cationic surfactant CPB	SWV	0.23–120.0	0.07	0.23	Mayonnaise, margarine, and biodiesel	[24]
PtE	SWV	30–100.0		-	-	[25]
Fe3O4- SWCNTs/1H3MITFB/CPE	SWV	0.008- 350.0	0.002	-	Drinking water and appel juices	[48]
AuNP-WC-GCE	SWV	0.005–0.075	0.0002	-	Soybean oil, blended oil, and red wine	[49]
CdO/SWCNTs-1,3- DPIBr-CPE	SWV	0.1–750.0	0.05	-	Sesame oil, soybean oil, and colza oil	[50]
FeNi3/rGO/HMPF6/CPE	SWV	0.05–900.0	0.01	-	Sesame oil, soybean oil and drinking water	[51]
Gold disc electrode	SWASV	25.27–490.3	6.14	20.45	Biodiesel samples	[52]
BC/GCE	SWV	-	-	-	-	[53]

Fig. 6 General fabrication scheme of AuNP-WC/GCE hybrid electrode in SWSV study for the determination of TBHQ [49]
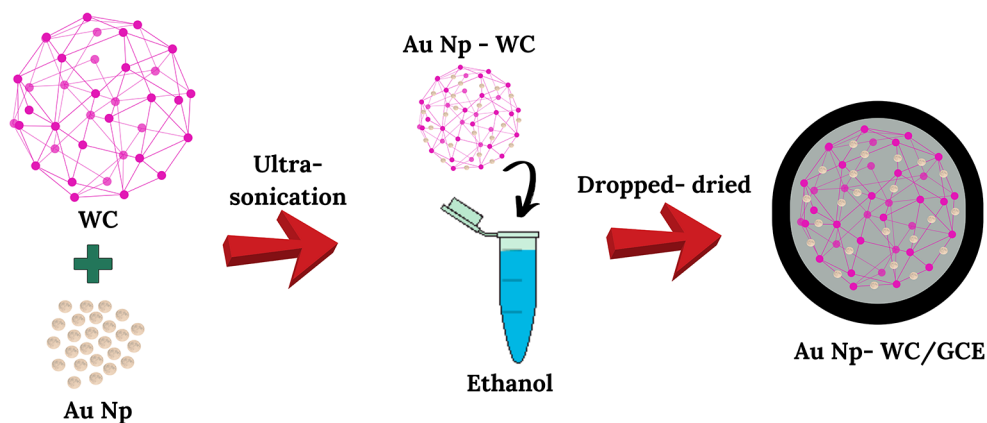
CV and LSV techniques

Cyclic voltammetry (CV) is a potentiodynamic technique in which the potential of the working electrode is increased linearly to a certain potential depending on the time and scanning rate, and the potential is scanned in the reverse direction to return to the initial potential. Because this situation resembles a triangular reversible voltammogram shape, it is referred to as cyclic. Meanwhile, the current value occurring on the electrode surface is the amount of change occurring between the working electrode and counter electrode, depending on the potential applied between the working electrode and reference electrode. In addition to taking a single measurement using the CV technique, numerous sequential data can be obtained, including facial measurements. Moreover, CV is frequently used electrochemical technique for investigating the reduction or oxidation processes of electroactive analytes. This technique is designed to examine the electrochemical properties of matter. This technique is designed to examine electrochemical properties such as whether the electrode reaction of the substance is reversible, how the substance transport type occurs, and elucidate the electrode mechanism, electrode reaction velocity, and kinetic model.

Although CV examines the qualitative properties of a substance, it is possible to conduct quantitative studies. There are studies conducted with CV in the literature, although few in number, regarding the determination of TBHQ. Looking at the four studies carried out with CV so far, a bare carbon fiber electrode (CFE) and some modified nanosensors have been used for TBHQ determination (Table 3). One, one study investigated the sensitivity of different ratios of silicon oxycarbide (SiCO)/GCE sensors developed at different annealing temperatures for TBHQ determination [54]. Moreover, in the study where bare CFE was used, TBHQ determination was successfully carried out using a capillary electrophoresis combine system combined with CV (CE-CV) [55]. Additionally, they obtained a very wide dynamic working range (7.5–1000 µM) with the CE-CV combined

analysis system and calculated an LOD value of 4.88 µM on the CFE. They determined the predictive accuracy and precision of CE-CV in TBHQ cosmetic products.

Considering the most sensitive work done with CV, they developed a new generation nanosensor, ZnTPP/MWCNT/ GCE, by coating the GCE electrode surface with zinc (II) tetraphenylporphyrin (ZnTPP) and MWCNTs with excellent conductivity [3] (Fig. 7). The surface morphology, structural characteristics, and conductive properties of the ZnTPP/MWCNT/GCE sensor were determined using SEM and TEM, XRD and FTIR, and electrochemical impedance spectroscopy. Additionally, they used a 5 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl to calculate the active surface area of the modified ZnTPP/MWCNT/GCE sensor using the Randles-Sevcik equation. Using biomimetic enzyme electrode with CV, they found the dynamic working range to be 0.01–1000.0 µM and the LOD value to be 27 nM in pH 7.0 phosphate buffer solution (PBS). They investigated the interference effect of various lipid antioxidants and different ions on the measurement results of TBHQ and determined TBHQ with high recovery in the presence of interfering substances. They also investigated the lifetime and repeatability of the developed nanosensor and demonstrated that the sensor was highly stable. Finally, they successfully determined TBHQ with high accuracy and precision in vegetable oils such as soybean oil and blended oil. Consequently, although the CV technique can be used to examine the electrochemical properties of a substance, it is a very fast, simple, and alternative quantitative technique for the determination of TBHQ.

Linear sweep voltammetry (LSV) is an analytical method in which the current change occurring between the working electrode and counter electrode is measured, while the potential between the working electrode and reference electrode increases linearly over time. In other words, LSV is called half-loop CV. The working principle is that LS voltammograms are obtained by scanning in one direction from the initial potential to the final potential according to anodic or cathodic scanning. LSV is
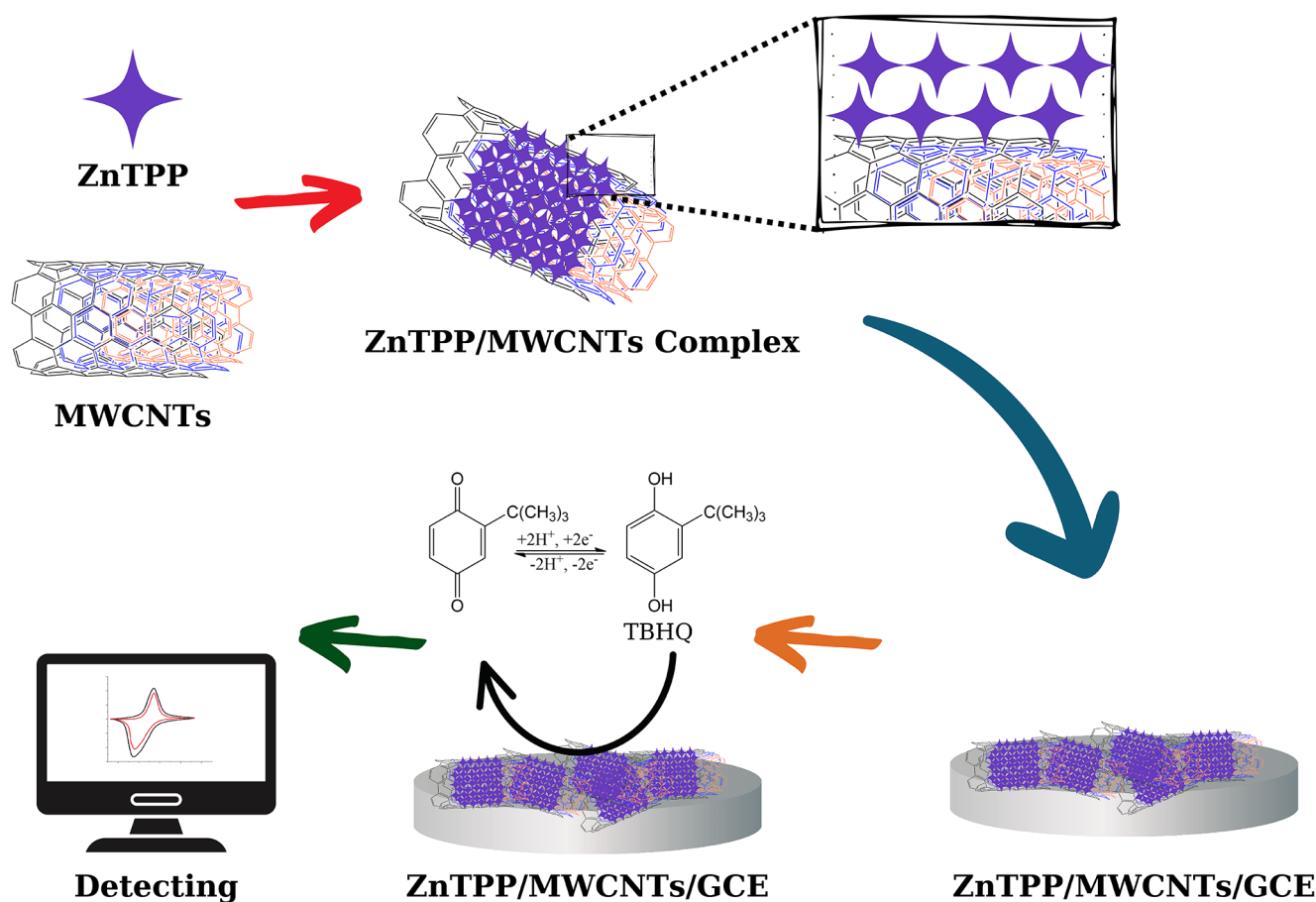
Fig. 7 General fabrication scheme of ZnTPP/MWCNTs/GCE electrode in CV study for the determination of TBHQ [3]

the simplest quantitative technique among voltammetric methods. Although LSV is not as sensitive as DPV and SWV, it is widely used in the determination of substances because it is simple and fast. In the literature, we come across very few studies using LSV in the determination of TBHQ (Table 3). They have developed modified sensors in all four studies carried out with LSV so far. Metal nanoparticle (Au-NP), carbonaceous material (MWCNTs), conductive polymer (poly(3,4-ethylenedioxythiophene, PEDOT), and poly(crystal violet) (PCV) nanomaterials as electro-catalytic activity were used to construct hybrid sensors in TBHQ determination by LSV. Although LSV studies recommended for TBHQ analysis were not sensitive compared to DPV and SWV studies, they were easily determined at µM levels in food samples. In addition, LSV, with the µM values of LOD, can compete with other analytical methods for TBHQ detection.

The Au NP/graphite electrode provided a significant increase in the anodic signal of TBHQ and exhibited catalytic properties by reducing its peak potential value [56]. The surface of the activated electrode was characterized using SEM. Using the TBHQ standard addition method on Au-NP/graphite electrode using LSV, they found the working range to be 4.81–481 µM and the LOD value to be 2.41 µM. They successfully implemented TBHQ analytics in samples such as ghee, sunflower oil and salad dressing. Finally, the synthetic antioxidants BHA, butylated hydroxytoluene (BHT), and TBHQ were determined simultaneously with LSV on the Au-NP/graphite electrode in pH 2 Britton-Robinson buffer solutions. Finally, they performed a statistical comparison with ultra-performance liquid chromatography (UPLC) to demonstrate the validity of the method.

Reviewing the most sensitive work performed by LSV, Tang et al., in their 2016 study, coated a PCV film onto the GCE surface via electropolymerization [57] (Fig. 8). The conductivity and surface morphology of the PVC/GCE electrode were characterized by EIS and SEM, respectively. The modified PCV/GCE exibited electrocatalytic activity with extraordinary sensitivity to the anodic signal of TBHQ. Furthermore, they calculated the active surface area of the modified PCV/GCE sensor by using the Randle-Sevcik equation in the $K_3[Fe(CN)_6]$ solution. They obtained a linear working range between 0.5 and 100 µM and calculated the LOD value as 0.03 µM in 0.1 M PBS at pH 7.0. They examined the selectivity of

Table 3 The mentioned CV and LSV analytical performances in the TBHQ determination

| Electrode	Method	Working range (µM)	LOD (µM)	LOQ (µM)	Analytical application	Ref
ZnTPP/MWCNTs/GCE	CV	0.01–1000.0	0.027	-	Soybean oil and blended oil	[3]
NiPcTs/PPy/PtE	CV	40–1800.0	23.1	43.6	Mushroom cream	[36]
SiCO/GCE	CV	-	-	-	-	[54]
CFE	Capillary electrophoresis coupled with CV	7.5–1000.0	4.88	26.1	Cosmetic samples	[55]
Au-NP/graphite	LSV	4.81–481.0	2.41	3.01	Ghee, sunflower oil and salad dressing	[56]
PCV/GCE	LSV	0.5–100.0	0.03	-	Corn oil, sesame oil, blend oil and soybean oil	[57]
MWCNTs/SPE	LSV	0.5–10.0	0.34	1.14	Soybean biodiesel samples	[59]
PEDOT: PSS/DMSO flexible electrode	LSV	0.5–200.0	0.15	-	Edible oils	[58]
CPE	LSV	1.05–10.15	0.071	0.237	Biodiesel	[60]
GDE	LSV	91.44-628.07	0.854	1.263	Pure mineral oil, biodiesel	[61]
GCE	LSV	6.01–90.24	0.439	-	Vegetable oil, solid food	[62]
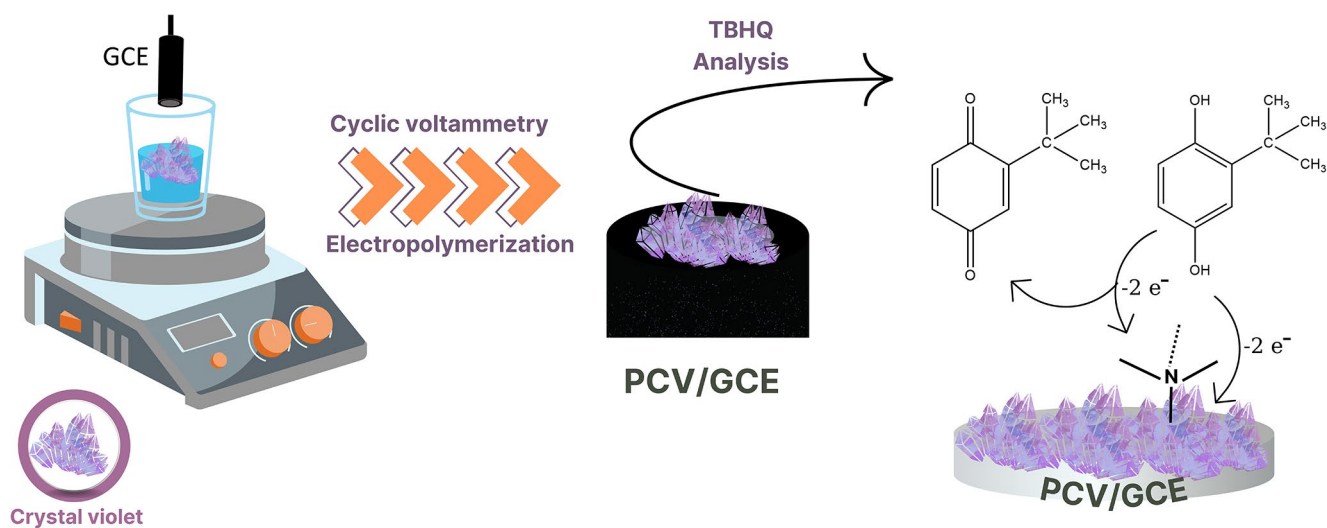
Fig. 8 General fabrication scheme of PCV/GCE in LSV for the analysis of TBHQ [57]

the proposed sensor LSV in the presence of citric acid, phthalate, vitamin E and various ions that are abundantly found in foods. To demonstrate the accuracy and precision of the developed electrode and the proposed nanosensor, they performed TBHQ analytical application on edible oil samples and performed TBHQ quantification by LSV on the PVC/GCE with high recovery (97.1 to 102%). They also compared it with HPLC techniques and found no significant difference between the two methods. As, as with other voltammetric techniques, LSV is one of the most important alternative methods for TBHQ determination in food samples.

In their study published in 2019, Tian et al. developed a copolymer-based poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) flexible voltammetric sensor for the determination of TBHQ (Fig. 9) [58]. The electron transfer efficiency of the indicator

electrode was increased by adding dimethyl sulfoxide (DMSO). To determine TBHQ, cetyltrimethylammonium bromide (CTAB), a cationic surfactant, was also used to improve mass transfer at the electrode-electrolyte interface. The surface morphology and structural properties of constructed PEDOT: PSS/DMSO flexible electrode were characterized by SEM, AFM, XPS, UV-vis and electrochemical analyses. They determined the linear operating response against the saturated calomel electrode (SCE) as 0.5–200 µM and determined the lowest detection limit in TBHQ analysis as 0.15 µM on flexible electrode by LSV. Finally, they successfully determined TBHQ in edible oils samples with low error and high recovery by LSV on PEDOT: PSS/DMSO flexible electrode. Consequently, they carried out the determination of TBHQ, an important food additive, with a fast, simple, cheap and practical sensor.
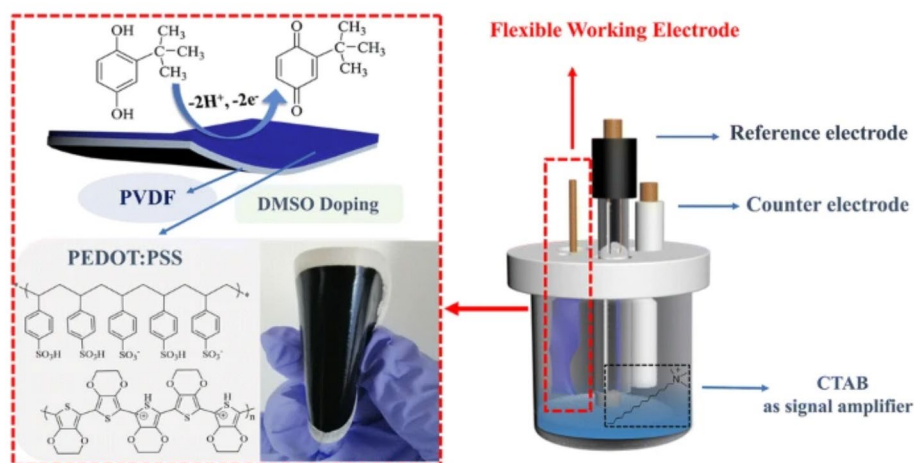
Amperometry

Amperometry is an electrochemical method based on measuring the current change occurring at a constant potential resulting from a redox reaction, such as the oxidation or reduction of an electroactive species. The word amperometry is derived from 'ampere', the unit of measurement of current, and 'meter', which is the measurement device. Therefore, amperometry has the most selective performance among the electrochemical methods. In addition, amperometry is widely used in quantitative analyses because the concentration of the analyte in the matrix environment linearly increases the resulting current intensity. Moreover, amperometry can be combined with different devices to further increase sensitivity and selectivity. The use of amperometry in combination with separation techniques such as chromatography, electrophoresis, and flow injection analysis allows for excellent simultaneous determination. In addition, analytes can be easily determined using amperometric titrations. However, the shortcoming of amperometry, which exhibits extraordinary performance, is that if oxygen is contained in the redox process, it must be removed from the environment using an inert gas such as nitrogen or argon. Owing to these unique features, amperometry is one of the two most preferred methods after DPV in the determination of TBHQ.

In amperometry studies, bare GCE, carbon screen-printed electrode (CSPE), carbon disc electrode, and various modified electrodes were preferred for the determination of TBHQ in food samples. Nanomaterials, nanomaterials with different properties such as metal oxide nanoparticles, carbonaceous materials, polymers and phthalocyanine have been used in the production of modified electrodes. AFM, BET, FE-SEM, Raman, SEM, and XRD methods were used
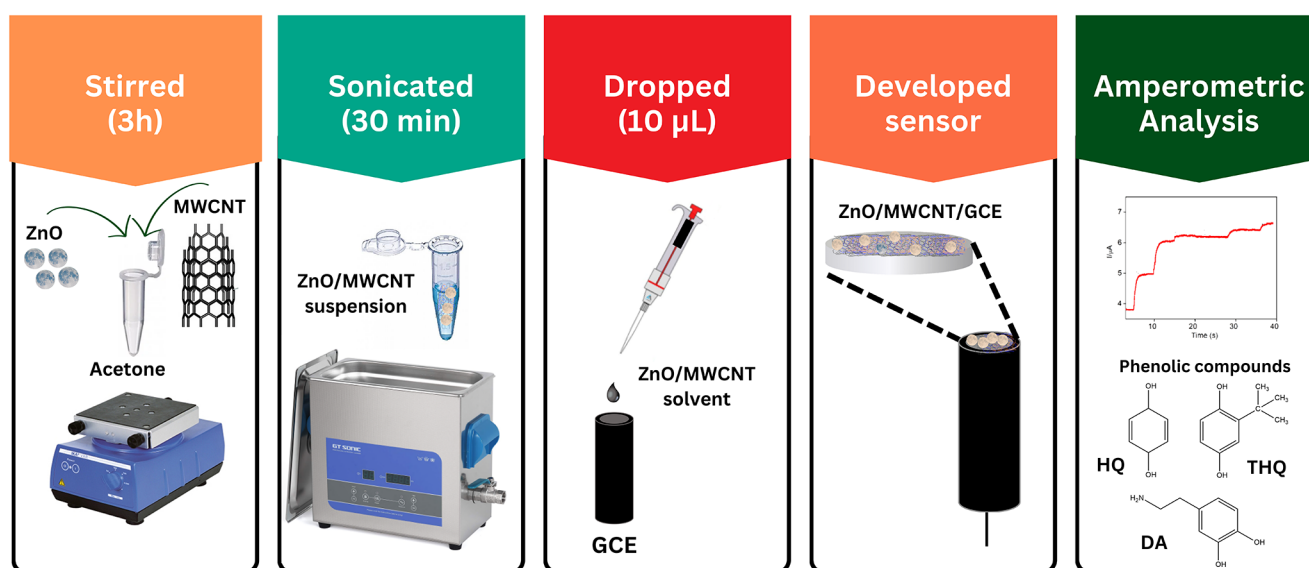

Fig. 10 Construction steps of ZnO/MWCNTs/GCE sensor for TBHQ analysis by amperometry [64]

for the surface morphology of the developed nanosensors while EIS and CV methods were used for the electrochemical activity and surface area of the modified sensors, respectively. Moreover, in studies conducted with amperometry, they developed nanosensors with very wide operating ranges and satisfactory LOD values that can be determined even in trace amounts. TBHQ determination at the micromolar and nanomolar levels in food samples can be easily performed using amperometry on the proposed nanosensor. In addition, selective analysis systems combining amperometry detector with methods such as flow injection analysis (FIA) and micellar electrokinetic capillary chromatography have also been developed for TBHQ analysis. As can be agreed from all these studies, in the determination of TBHQ, amperometry is an important alternative candidate analysis method such as electroanalytical methods in food samples due to its high accuracy, precision and, low LOD values.

Considering the studies conducted on amperometry, it is understood that it has sensitivity that can compete with other traditional analytical methods. In addition, amperometry can be used very easily in routine analyses of TBHQ because it is fast, simple, cheap and does not require pre-treatment. The use of amperometry as an excellent detector, even in electrophoresis and FIA systems a significantly contributes to the quantitative analysis of TBHQ in food samples. In, in amperometric studies, nanomaterials have been used to increase the sensitivity of the indicator electrode, with carbonaceous materials being the primary ones. These hybrid nanosensors noticeably improved not only the sensitivity of the electrode but also its catalytic performance. Considering the most sensitive study performed using amperometry, Lima et al. coated a GCE indicator electrode surface with α-Al$_2$O$_3$ nanoparticles [63]. The α-Al$_2$O$_3$/GCE nanosensor increased the anodic signals of catechol (CT), dopamine and TBHQ 10-fold in amperometric measurements. They

investigated the surface morphology and structural form of the nanosensor developed for the determination of TBHO by using AFM, FE-SEM, BET, X-ray diffraction, and CV methods. They found the linear working range for TBHQ to be 0.5–250 μM and the LOD value to be 0.027 μM with amperometry combined with batch injection analysis (BIA) on the α-Al$_2$O$_3$/GCE nanosensor in 0.1 M HClO$_4$. In conclusion, this sensitivity demonstrates that amperometry is as sensitive as other electrochemical techniques in THHQ determination. In addition, the sensor shows that it can be easily used for the simultaneous determination of α-Al$_2$O$_3$/GCE nanosensor, which have a wide working range, high selectivity and repeatability. In another sensitive study, Freire et al., first trapped, ZnO nanoparticles were trapped inside MWCNT under stirring in acetone [64] (Fig. 10). The obtained ZnO/MWCNT colloidal solution was applied to the cleaned GECE surface using the drop-dry technique and the ZnO/MWCNT/GCE indicator electrode was constructed for the TBHQ determination. While they examined the surface morphology using SEM, they investigated the electroactivity and active surface area using CV and EIS, respectively. They then examined the anodic signals of three phenolic compounds, dopamine, hydroquinone (HQ), and TBHQ, and found that the modified ZnO/MWCNT/GCE electrode increased the signal of substances by approximately 4-fold compared to the bare GCE. They found a linear working range for the determination of TBHQ on ZnO/MWCNT/GCE by amperometry at 2-1000 μM and calculated the LOD value as 0.08 μM (80 nM). Consequently, they developed an amperometric sensor with high stability, excellent sensitivity and very fast speed for the determination of TBHQ and other phenolic compounds. In conclusion, amperometric studies show that TBHQ determination can be performed very easily and can easily compete with other traditional methods on the nanosensors(Table 4).

Table 4 The mentioned amperometry analytical performances in the TBHQ determination

Electrode	Method	Working range (μM)	LOD (μM)	LOQ (μM)	Analytical application	Ref
α-Al$_2$O$_3$/GCE	Amperometry with BIA	0.5–250.0	0.027	-	-	[63]
ZnO/MWCNTs/GCE	Amperometry	2.0–1000.0	0.08	-	-	[64]
Poly(carminic acid)/MWNT/ GCE	Amperometry	0.50–75.0	0.36	-	Linseed oil	[65]
GCE	Amperometry	60–600.0	5.0	-	Biodiesel	[66]
NiPcTs/PPy/GCE	Amperometry in FIA	3.2–32.0	0.26	0.86	Fish broth tablets	[67]
Carbon disc electrode	MECC–ED as amperometry	2.0-500.0	0.8	-	Facial mask, bath oil, and moisturing sun block lotion	[68]
SD-MWCNTs/GCE	Amperometry	0.5–1000.0	0.33	-	-	[69]
CSPE	Amperometry	1.0-1000.0	0.18	-	-	[70]
GCE	MPA-FIA	2.0-100.0	-	2.51	Chewing gum	[71]
GCE	MPA-BIA	1.0-1000.0	0.075	-	Biodiesel	[72]
GCE	Amperometry	2.50–1000.0	0.64		Extracts of linseed oil	[73]

Table 5 Photoelectrochemical (PEC) platform in analytical performances for the determination of TBHQ

Electrode	Method	Working range (μM)	LOD (μM)	LOQ (μM)	Analytical application	Ref
LiTCNQ-TiO$_2$/ITO	PEC	0.6–5000.0	0.17	-	Cosmetic samples	[74]
CdSe/ZnS/LiTCNE/ITO	PEC	0.6–250.0	0.21	0.70	Babassu oil, soybean oil	[75]
LiTCNE-TiO$_2$/ITO	PEC	0.4–500.0	0.010	-	Biodiesel samples	[76]
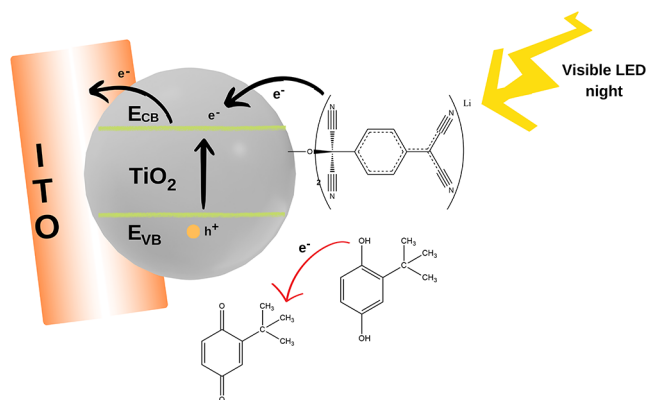
Fig. 11 Suggested mechanism for the PEC determination of TBHQ with the LiTCNQ-TiO$_2$/ITO [74]

Photoelectrochemical (PEC) platform

The branch of science that studies the oxidation or reduction reactions occurring at the electrode interface under the irradiation of a system containing an electroactive substance and photosensitive material is called photoelectrochemical (PEC). In the photoelectrochemical technique, the change in the signal (electric current) occurring in the analyte due to excitation (radiation) was examined. Particularly on the PEC platform, it enables the detection of a wide variety of analytes on semiconductors such as indium tin oxide (ITO). For TBHQ determination, sensors coated with nanomaterials on the ITO electrode surface have been developed. These materials include TiO$_2$, which has extraordinary catalytic properties. Looking at the study with PEC for TBHQ, they have a wide working range and LOD value at μM levels. The sensitivity achieved with PEC is comparable to those of other electrochemical and traditional analytical methods. Moreover, because it is fast, simple, and low-cost, PEC has attracted attention in recent years, not only for the determination of synthetic phenolic compounds, such as TBHQ, but also for the production of numerous nanosensors for the analysis of amino acids, DNAs, and other substances (Table 5, Fig. 11).

Conscluion

Tert-butyl hydroquinone (TBHQ), a member of SPA, is one of the preservative food additives. TBHQ is widely used as an additive in food and vegetable oils, as well as in the pharmaceutical and cosmetic industries, due to its low cost and high chemical stability. However, because TBHQ causes serious diseases when taken in high doses, fast, reliable, and sensitive analytical methods are required for the determination of such substances in food products. Although classical analytical methods have been used, electrochemical methods are widely preferred for the determination of TBHQ because of their extraordinary features, such as speed, reliability, sensitivity, and no need for pretreatment. The most commonly used electrochemical methods for TBHQ determination are SWV, DPV, CV, PEC and amperometry in TBHQ determination. In previous research conducted thus far, nanosensors utilized as indicator electrodes have been categorized, and it has been observed that carbon nanosensors are particularly favored in the fabrication of working electrodes. In this review, the validation parameters, specifically the working range and limits of detection (LOD and LOQ) of the sensors, were evaluated, and the sensitivities of the electrochemical methods were compared to those of other classical analytical techniques. The various electrochemical methods developed for determining TBHQ in food samples have demonstrated sensitivity that is comparable to that of chromatographic and spectrophotometric methods. Finally, food samples where TBHQ was detected, especially vegetable oils, were classified in detail. Consequently, the strategies of electrochemical methods and nanosensors developed for the analysis of TBHQ in food samples were found to be highly predictive of analytical performance with high accuracy, selectivity, sensitivity, recovery, and low relative error.

Future perspective

Tert-butyl hydroquinone (TBHQ), a synthetic phenolic antioxidant, is widely used as a preservative in foods, oils, and other substances. However, if consumed over daily intake doses, it is known to cause diseases such as DNA damage [7], carcinogenesis [8], and cell apoptosis [9, 10]. Some countries have restricted or banned the use of TBHQ [18]. Therefore, detecting TBHQ in food is of great importance, as it negatively affects human health. In addition, analyses of these substances must be performed routinely. Although traditional methods have been frequently used to detect TBHQ in food samples, new analytical methods with high sensitivity, fast analysis time, portability, and low cost are still required. Therefore, electrochemical techniques and

nanosensors for TBHQ analysis have attracted significant attention.

Because the hydroxyl (-OH) functional groups in the TBHQ structure can be easily oxidized to quinones, electrochemical studies have been performed [21]. Thus far, techniques such as DPV, SWV, LSV, CV, amperometry, and PEC have been used in electrochemical studies for the analysis of TBHQ in foods. So far, different nanosensors, mainly carbonaceous materials, have been used in rapid and sensitive studies to determine TBHQ. However, although the electrochemical properties and electrode mechanisms of TBHQ have been elucidated, the development of more sensitive nanosensors for the detection of TBHO in complex matrices is open from a future perspective. In addition, these new studies will lead to the development of portable devices for electro-active substances by electrochemical methods. Also, there is a need for the simultaneous determination of such substances or metabolites by developing more selective and sensitive electrochemical techniques, such as the ability to determine many substances simultaneously, which is an advantage over other traditional methods. Thus, trace amounts of TBHQ can be easily determined using new-generation nanosensors in food samples. The development of electrochemical systems combined with traditional analytical methods used in the TBHQ tray will be one of the important areas of future work. Consequently, although the work done so far in TBHQ determination numerically excessive, more sensitive sensors or devices for portable, on-site analysis will be needed with nanomaterials to be discovered in the future.

Abbreviations

μM	Micromolar
1H3MITFB	Hexyl-3-methylimidazolium tetrafluoroborate
ADC	Azodicarbonamide
AFM	Atomic force microscopy
AgNPs	Silver nanoparticles
AuNPs	Gold nanoparticles
BC/GCE	Biochar modified glassy carbon electrodes
BET	Brunauer, Emmett and Teller method
BHA	Butyl hydroxyanisole
BHT	Butylated hydroxytoluene
BIA	Batch injection analysis
CB	Carbon black
CBPE	Carbon black paste electrode
CE-CV	Capillary electrophoresis combine system combined with CV
CFE	Carbon fiber electrode
CFME	Carbon fiber microelectrode
CNTs	Carbon nanotubes
CPB	Cetylpyridinium bromide hydrate
CPE	Carbon paste electrode
CSPE	Carbon screen-printed electrode
CT	Catechol
CTAB	Cetyltrimethyl-ammonium bromide
CuTSPc	Copper (II) tetra sulfonated phthatocyanine
CV	Cyclic voltammetry
DMSO	Dimethyl sulfoxide
DPV	Differential pulse voltammetry
EDX	Energy-dispersive ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ERGO	Electrochemically reduced graphene oxide
FCB	Functionalized carbon black
FDA	US Food and Drug Administration
FE-SEM	Field emission scanning electron microscope
FIA	Flow injection analysis
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GCE	Glassy carbon electrode
GPE	Graphite paste electrode
Gr	Graphene
GRE	Graphite rod electrode
HMPF6	n-hexyl-3-methylimidazolium hexafluoro phosphate
HPLC	High-performance liquid chromatography
HQ	Hydroquinone
HR-TEM	High-resolution TEM
ITO	Indium tin oxide
LiTCNQ	Lithium 7,7',8,8'-tetracyanoquinodimethanide
LOD	Limit of detection
LSV	Linear scanning voltammetry
MB	Methylene blue
MBIBr	n-methyl-3-butylimidazolium bromide
MECC?ED	Micellar electrokinetic capillary chromatography - electrochemical detection
MIP	Molecularly imprinted polymer
MLLE	Micro liquid-liquid extraction
MOF	Metal organic framework
MPA	Multiple-pulse amperometry
MWCNTs	Multi-walled carbon nanotubes
NC	Nano composites
NCNTs	Nitrogen-doped carbon nanotubes
NiPcTs	Tetrasulfonated nickel(II) phthalocyanine complex
nM	Nanomolar
NRs	Nano rods
P3MT	Poly(3-methylthiophene)
PBS	Phosphate buffer solution
PCV	Poly(crystal violet)
PDG	Poly(D-glucosamine)
PEC	Photoelectrochemical

PEDOT	Poly(3,4-ethylenedioxythiophene)
PG	Propyl gallate
PLA	Poly(lactic acid)
POM	H3PW12O40
PPy	Polypyrrole
PSS	Poly(styrenesulfonate)
PtE	Platinum Electrode
PVP	Poly(vinylpyrrolidone)
rGO	Reduced graphene oxide
RSD	Relative standard deviation
SCE	Saturated calomel electrode
SD	Small diameter
SEM	Scanning electron microscopy
SiCO	Silicon oxycarbide
SPA	Synthetic phenolic antioxidant
SPCE	Screen-printed carbon electrode
SWASV	Square-wave anodic stripping voltammetry
SWCNTs	Single-walled carbon nanotubes
SWSV	Square wave stripping voltammetry
SWV	Square wave voltammetry
TBBQ	Tert-butylbenzoquinone
TBHQ	Tert-butyl hydroquinone
TEM	Transmission electron microscopy
TGA	Thermogravimetric analyzer
TMO	Ternary metal oxide
WC	Tungsten carbide
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZC	ZIF-8 derived nanoporous carbon material
ZnTPP	Zinc (II) tetraphenylporphyrin
β-CD	β-cyclodextrin

Declarations

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