Review

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ELECTROANALYSIS

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Electrochemical Detections of Tea Polyphenols: A Review

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Abstract: Tea, contains an abundant amount of polyphenols, has many health benefits, and acts as a remedy for many diseases, including cardiovascular and neurological disorders. In this article, we have reviewed the reported electrochemical techniques for the detection of tea polyphenols under the sub-headings, separation coupled with electrochemical detection, direct electrochemical detection, bioelectrochemical sensing, simultaneous electrochemical detection and flow injection analysis.

Keywords: Tea polyphenols · electrochemical sensor · chemically modified · electrode · biosensor · tea-real sample analysis

1 Introduction

Tea is the historic refreshment in the world, alongside water, due to its rich aroma, taste and health benefits. Consumption of tea is found to minimize the risks of carcinoma [1], Alzheimer's [2] and Parkinson's disorders [3], arthritis [4], carcinogenic, cardiovascular, neurological and other infectious diseases [5] due to the pharmacological nature of its constituents. The different varieties of tea, namely green tea, oolong tea, black tea, are all extracted from the dried leaves and buds of the plant named *Camellia sinensis.* These varieties differ in the nature of physical withering, fermentation condition, processing nature and time [6–8]. All the types of tea contain more or less the same constituents, but the point at which they differ is the fermentation process. The green tea, which looks light in color is a non-oxidized product, but the black tea is allowed to oxidize in the presence of air, which makes it dark in color, due to the condensation polymerization of catechins to produce theaflavin (TF) and theobromine (TR) [8–9]. A normal cup to freshly brewed tea consists mostly of polyphenols of about 30–40 %, especially catechins (CE), epicatechin-3-gallate (ECG), epigallocatechin-3-gallate (EGCG), gallocatechin (GC), epicatechin (EC), epigallo catechin (EGC), catechin gallate (CG), gallocatechin gallate (GCG) in significant quantities and minor amounts of epigallocatechin digallate, methylepicatechin and methyl EGC (Scheme 1) [10]. The oolong tea, contains almost the same constituents as green tea, but it is semi-fermented (that is, it is 20 to 60 % oxidized). Green tea is rich in EGCG, whereas, the black tea is rich in TF. The presence of higher content of polyphenols gives the tea, astringency and bitterness. Apart from the above constituents, flavonols like myricetin, kaempferol, quercetin, and their glycosides are also present in tea. The factors which affect the quality of tea includes the place of cultivation, soil nature (pH, moisture content, nutrient availability, fertility), climatic change, type of fertilizers used etc [11]. The presence of a variety of polyphenols as antioxidants helps in entrapment of free radicals, which are generated through different body metabolisms and by inhibiting the initiation of cancer cell formation (Scheme 2) [12]. Note that the green tea catechins are recognized as 1,2-dihydroxybenzene (1,2-DHB), 1,3-dihydroxybenzene (1,3-DHB), and 1,2,3-trihydroxy benzene (1,2,3-THB), which are derivatives of the polyphenols (Scheme 1). EGCG is found to contain 1,2,3-THB predominantly, which is responsible for the antioxidant property. Hence, a selective, sensitive and quick detection of tea polyphenols is a challenging research concern in analytical chemistry.

In general, the tea quality is assessed with the simple testing of smell and taste by a human tongue, but the quantitative analysis cannot be pursued in the same way. There are various electrochemical techniques available for the determination of the constituents of tea, based on which this review article has been structured, with the database containing 39 papers in the past 20 years (2000–2020) from Scopus indexed journals with keywords in the titles, "Electrochemical sensing and Tea". The title has been separated into five major topics, based on the method of determination of tea constituents, which are as follows: (1) Separation coupled electrochemical detection of tea constituents, (2) direct electrochemical detection of tea constituents, (3) bio-electrochemical sensing of tea constituents, (4) simultaneous electrochemical detection of multi-constituents by non-separation method and (5) flow injection analysis coupled electrochemical detection of tea polyphenols (Scheme 3). While considering the case of separation techniques, chromatography has been popularly used for the determination of tea constituents. Each and every component of tea can be separated with its action with the mobile and stationary phase of the

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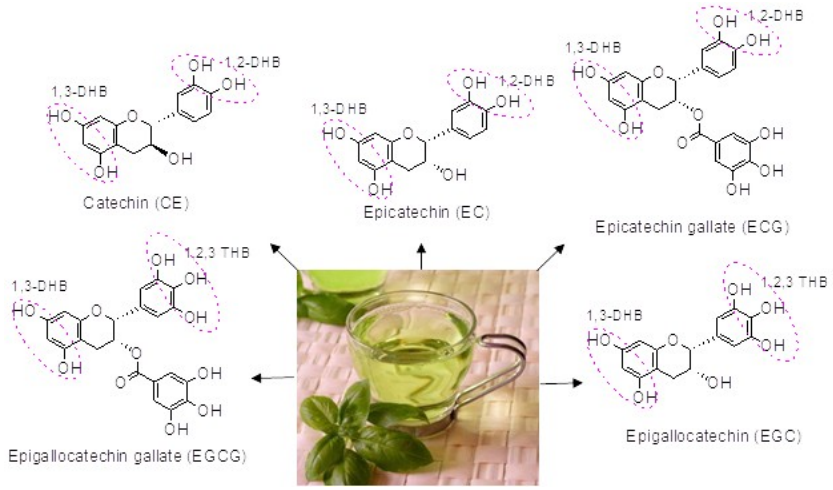

Scheme 1. Structural aspects of major tea polyphenols. Copy right will be obtained from Royal Society of Chemistry Journal. Reprinted with permission from the RSC publisher [Ref. No. 51].

column. After segregation, the ingredients are analyzed using conventional detection techniques such as UV-visible spectrometer [13–15], mass spectrometry [16–18] and electrochemical detection [19–20]. When electrochemical detection combines with chromatography, it helps in sensitive and selective detection of polyphenols, even when they are present in trace amounts. However, non-volatile components require liquid chromatography, and volatile components require gas chromatography for the best analysis. Since the segregation and analysis of tea components are done separately, it becomes a tedious and time-consuming process of detection. Thus, a simpler and quick analysis technique was required for the detection of tea polyphenols. Here comes the electrochemical technique, which attracted many researchers due to the ease in the preparation of chemically modified electrodes

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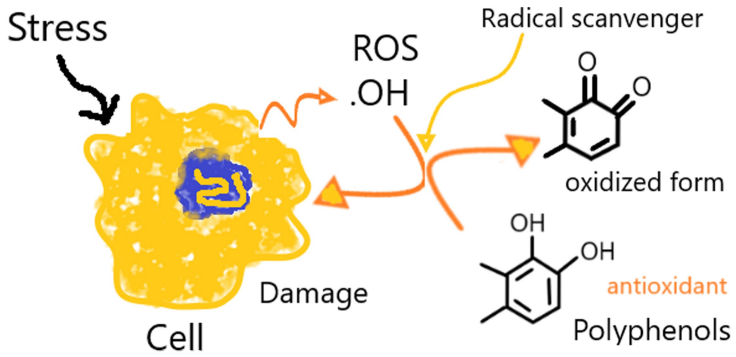


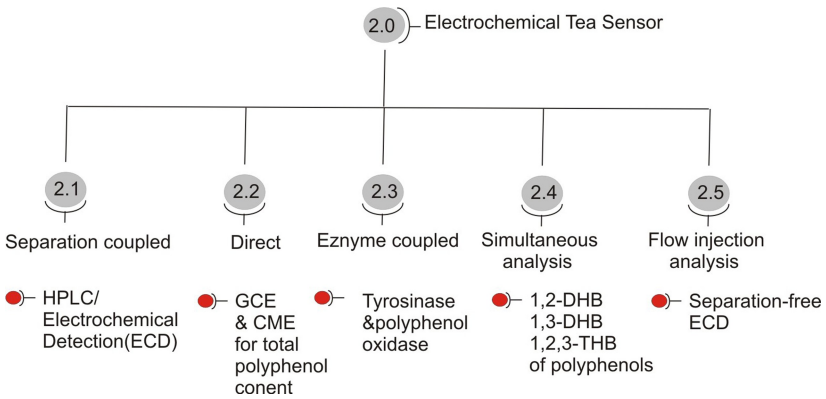
Scheme 2. Illustration for the mechanism of antioxidant behavior of polyphenols. The reactive oxygen species (ROS) like hydroxyl radical (·OH) generated at the time of cellular stress- condition is removed by the polyphenols via the redox mechanism. The scheme is drawn by the corresponding author.

(CMEs), rapid analysis, less consumption of the analysis sample volume. Recently, in 2020, Martin et al., reported the electrochemical analysis of tea using sensors, as a book chapter [21]. Several methods, such as electrochemical and bioelectrochemical sensors, electronic-tongue, and its biosensors for the analysis of tea polyphenols, have been briefly described by the authors. Note that the electronic tongue is referred to as a human tongue in consideration with selective analysis of the target chemical. This kind of electronic device contains multisensory arrays to detect the various physical properties and from pattern recognition, the target chemical is selectively detected. Considering the broad spectrum techniques in the determination of tea constituents, this review article aims to identify the polyphenols present in tea. The salient features of all the techniques have been discussed here.

2 Classification of Different Techniques for the Detection of Polyphenols

2.1 Separation Coupled Electrochemical Detection of tea Constituents

There are several reports available for the determination of tea constituents separately, using high-pressure liquid chromatography (HPLC) in association with the electrochemical detector (ECD) system. The dihydroxybenzene components of tea can be electro-oxidized using carbon-based commercial electrodes and analyze the catechin and its derivatives sensitively and selectively. The real samples which are used in the separation and detection of tea polyphenols are either tea infusions or human samples (plasma, urine, serum etc.). In this section, we have listed out the works, which includes the utilization of real samples, under two subcategories, namely, tea infusions and human samples as real samples (Table 1).



Scheme 3. Various classifications of electrochemical sensors proposed.

Table 1. Literature collection for the HPLC coupled electrochemical detection of tea polyphenols.

Analyte/s	Mobile Phase	Potential vs Ag/AgCl	pH	Real samples	Flow rate	Ref.
Catechins	Sodium dihydrogen phosphate (0.1 M) + 0.1 mM EDTA·2Na : acetonitrile (87 : 13)	0.6 V	2.5	Tea infusions	1.0 mL min^{-1}	[22]
Polyphenols	Chloroacetic acid (20 mM) + acetonitrile (11 %)	0.4 V 0.9 V	2.8	Tea infusions		[23]
Polyphenol as antioxidant capacity	No analytical column	0.6 V		Tea infusions	0.8 mL min^{-1}	[24]
Catechins	Acetonitrile : phosphate buffer solution (0.1 M) (15 : 85 v/v)	0.6 V	5.5	Human urine	0.45 mL min^{-1}	[25]
Catechins	Phosphoric acid (50 mM) + EDTA (0.05 mM) + acetonitrile (14 %)	0.6 V	2.5	Human plasma	1.0 mL min^{-1}	[26]
Catechins	Deaerated phosphoric acid : water : methanol (0.5 : 81 : 19, v/v/v)	0.6 V	3.6	Human plasma	0.025 mL min^{-1}	[27]
Quercetin	Deaerated methanol : water mixture 4 : 6, v/v) + 0.5 % phosphoric acid	0.5 V	5.0	Human plasma	0.025 mL min^{-1}	[28]
Catechins and Gallic acid	Phosphate buffer : acetonitrile (99 : 1) and (77 : 23)	0.25 V	2.5	Human serum	1.0 mL min^{-1} to 1.5 mL min^{-1}	[29]

2.1.1 Tea Infusions as Real Samples

In 2001, Sano et al., reported the determination of twelve catechins (four major tea components, four epimers and four methyl catechins) using HPLC-ECD technique [22] (Table 1). The tea infusions were prepared by mixing 50 grams of tea powder in acetonitrile : distilled water (1 : 1), and the supernatant liquid was filtered and taken for analysis. The HPLC column was kept at 30 °C inside an oven. The mobile phase, which was used in the HPLC column, consists of sodium dihydrogen phosphate buffer (0.1 M, pH 2.5) containing EDTA·2Na : acetonitrile (87 : 13) with 1.0 mL min^{-1} flow rate. The applied potential was 0.6 V (vs Ag/AgCl) for the electrochemical detection of tea catechins. They also compared the tea infusions prepared using water : acetonitrile (1 : 1) with that of hot water and reported that the former solvent inhibited the epimerization of catechins. In 2001, Long et al., separately analyzed eight catechins using liquid chromatography with a multi-channel amperometric detector [23]. The tea infusions prepared by brewing tea leaves in hot water and extraction in 50 % and 100 % of methanol were compared and found that the tea infusion made by brewing (also known as infusion method) had the highest efficiency of extraction. An electrochemical detector with four working electrodes was used for the detection. Each electrode was set up at different potentials and the analyte of the same concentration was allowed to flow through all the four electrodes. In the year 2011, Andlauer et al. opted rapid electrochemical screening technique for the determination of antioxidant power of selected tea samples [24]. In the above study, a programmable commercial ECD was used without an analytical column. The samples were injected with Trolox solution in the buffer, with a flow rate of 0.8 mL min^{-1} and 0.6 V (vs Ag/AgCl) as an operating potential for ECD. The results were compared with 2,2-diphenyl-1-picrylhydrazyl (DPPH) and ferric reducing antioxidant power (FRAP) assays. They reported that the method was well suited for altering the antioxidant power during the growth or storage of food plants.

2.1.2 Human Samples as Real Samples

In 2000, Yang et al., reported the utilization of HPLC-ECD for the determination of catechins in human urine using EDP-1 commercial electrochemical detector, by oral ingestion of canned green tea, after 1 to 3 hours of absorption in bloodstream [25]. The collected urine sample was thawed and mixed with phosphate buffer solution, sodium dihydrogen phosphate containing ascorbic acid : EDTA·2Na mixture (20 : 0.1) along with β-glucuronidase and sulfatase. For about 45 minutes, the above mixture was kept at an incubation temperature of 37 °C. The above solution was filtered and injected in the HPLC column. They found CE, EC, GC and EGC to be present in the urine sample after the consumption of tea. Further, in 2001, Umageki et al., recorded the detection of catechins in human plasma using HPLC, with commer-

cial Coulochem II (ESA Inc., Bedford, MA, USA) as a guard cell for the electrochemical detector. In the typical electroanalysis, the human plasma was mixed with acetonitrile in 1:1 ratio for the protein to precipitate, and then catechin containing liquid was subjected to analysis by solid-phase extraction [26]. To analyze the catechins in their conjugated forms, glucuronidase, along with sulfatase were added to the plasma sample (incubated at 37 °C for 45 minutes) and the detection was executed. Similar to the previous method, in 2003, Kotani et al., carried out almost the same procedure to detect human plasma catechins using HPLC-ECD with LC-4 C electrochemical detector (trade name) [27]. The setup consisted of an octadecyl silica column (ODS), maintained at 40 °C, through which the test sample had been eluted. A mixture of phosphoric acid:water:methanol (v/v/v of 0.5:85:19) was used as the mobile phase (flow rate 25μL min^{-1}). The ECD was operated at a potential of +0.6 V vs Ag/AgCl. The catechins in human plasma were detected after the intake of a commercially available canned tea. The obtained plasma sample was made into a mixture with pH 3.6 phosphate buffer containing ascorbic acid, EDTA·2Na along with pH 6.8 phosphate buffer containing glucuronidase and sulfatase. Ethyl gallate was used as an internal standard. The above-prepared mixture was kept at an incubation temperature of 37 °C for about 45 minutes. The catechins from the above mentioned enzyme-hydrolyzed solution was separated using ethyl acetate, dried and dissolved in the mixture of above mentioned mobile phase. The test sample was injected into the HPLC column. The above method of HPLC-microbore column was found to be highly sensitive for the detection of catechins in human plasma. In 2004, Jin et al., detected quercetin in the human plasma through semi-micro HPLC-ECD, by the oral ingestion of the commercially available canned tea [28]. The human plasma was mixed with acetate buffer of pH 5.0, which contained ascorbic acid, along with the mixture of β-glucuronidase, sulfatase and the internal standard luteolin and incubated at 37 °C for about 3 hours. The extract was collected using ethyl acetate and dried using nitrogen stream. The dried remaining was dissolved in a mixture of methanol:water (4:6 v/v), which contained a portion of phosphoric acid. The above-prepared test sample was injected in HPLC-ECD and analyzed. Ion-pair HPLC-ECD with commercial coulochem III detector was used in the year 2014 by Narumi et al., for the detection of gallic acid and catechins simultaneously, present in human serum samples after the intake of tablets of green tea [29]. The test sample was prepared similarly as mentioned by Kotani et al. The catechins were deconjugated using freshly prepared glucuronidase and sulfatase, and the concentration of free catechins and gallic acid were analyzed. They reported that this method was useful for estimating the kinetics and health benefits of catechins after the consumption of tea.

2.2 Direct Electrochemical Detection of Tea Constituents

Antioxidants are a special class of compounds that inhibits/quenches the oxidation process and radical species generated in body cells. The hydrogen peroxide, hydroxyl radical and superoxide anion are the most commonly found reactive oxygen species (ROS) in the human body. The polyphenols, which come under the classification of non-enzymatic antioxidants, helps in the scavenging action of those ROS, by in turn, preventing the disruption of body cells. Thus, it is crucial to detect antioxidants qualitatively and quantitatively [12]. In the literature reports, a single compound or mixture of tea polyphenols was focused on the detection. In 2010, Žegarac et al., utilized an unmodified glassy carbon electrode (GCE) for the detection of tea polyphenols in terms of antioxidant capacity in tea infusions of commercially available flavored fruit teas in acetate buffer (pH = 3) [30]. They reported that 1,2,3-THB and gallate functional groups were responsible for the antioxidant capacity of the tea infusions. Among the infusions they analyzed, rosehip containing fruit tea was found to exhibit a higher antioxidant capacity index and a prominent peak with $E_p = +0.44$ V, corresponds to the existing of 1,2,3-THB and gallate groups. The above method was compared with the standard DPPH, FRAP and decay of the radical cation ABTS (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate)) assays, which showed a positive correlation. In 2016, Karaosmanoglu et al., reported the analysis of phenolics in dilute tea and coffee infusions using poly(3,4-ethylenedioxithiophene) (PEDOT) polymerized GCE in pH 5.5 phosphate buffer solution (PBS) [31]. The prominent phenolics, which were initially identified using HPLC, were studied using the CME and compared with the spectrophotometric Folin Ciocalteu assay. In 2017, Ziyatdinova et al., reported the determination of the antioxidant capacity of tea samples using chronoamperometry technique. The CME used here was quercetin polymerized over multiwalled carbon nanotubes (MWCNT) modified GCE (designated as GCE/MWCNT/PQ), in pH 7 PBS [32]. The oxidation potentials of tea antioxidants viz., gallic acid (GA), EGCG, quercetin, rutin, CE and tannin, using differential pulse voltammetry (DPV) technique. Chronoamperometry technique was used at a potential of +0.2 V for the estimation of antioxidant capacity. The same group, in 2017, reported the estimation of GA, EGCG and CE using the same CME, GCE/MWCNT/PQ (PQ-polyquercetin), using DPV in pH 7 PBS [33]. The CME was extended to green, white, oolong and black teas as real samples. In 2018, Deutchoua et al., reported a DPPH modified carbon paste electrode (CPE) for the analysis of the antioxidant properties in real samples in pH 7.0 PBS [34]. They initially used ascorbic acid as a standard, and further extended it to commercially available tea sample infusions. They found that the DPPH of the modified electrode, quenched the antioxidants present in the tea sample, which was indicated by the reduction in the

Table 2. Literature collection for the various chemically modified electrodes available for the electro analysis of tea constituents (polyphenol) by various electrochemical techniques.

CME	Analyte/s	Tech.	Potential	pH	Detection limit	Real samples	Ref.
1.GCE	Polyphenol as antioxidant	CV	0.4 V	3.0[b]		Blueberry, peach and tangerine, pink grape, apple and cinnamon, orange, rose hip, forest fruit, apricot, cherry and strawberry flavored teas	[30]
2.GCE/PEDOT	Total phenolic content	CV	0.5 V	5.5[a]		Diluted tea and coffee infusions	[31]
3.GCE/MWNT/PQ	Polyphenol as antioxidant	Chrono-amperometry	0.2 V	7.0[a]	0.063 μM	Green, white, semi-fermented and black teas	[32]
4.GCE/MWNT/PQ	GA CE EGCG as Antioxidants	DPV	0.15 V	7.0[a]	 0.10 μM 0.024 μM 0.014 μM	Green, white, oolong and black teas	[33]
5.CPE/DPPH1 %	Polyphenol as antioxidant	CV	0.8 V	7.0[a]		Commercial tea brands	[34]
6.GCE/PANI/DNA-NR GCE/PANI/DNA-MB GCE/PANI/DNA-MG	Polyphenol as antioxidant	CV	0.5 V	6.0[a] 7.0 8.0		Commercial tea brands	[35]
7.SPME	Polyphenol as antioxidant	DPV	0.3 V	7.0[a]	0.2 mM	Black and green tea	[36]
8.GCE/fMWCNT/YHCF	Catechin	CV	0.3 V	6.0[a]	0.28 μM	Green tea, Oolong tea	[37]
9.GCE/fMWCNT/MnO_2/Pt	Catechin	CV	0.2 V	6.5[a]	0.02 μM	Red wine, green tea, black tea	[38]
10.GCE/Chloramine T SPE/Chloramine T PtE/Chloramine T	Catechin	Amp i–t	0.45 V 0.417 V 0.414 V	6.8[a]	1.569 mg L^{-1} 0.674 mg L^{-1} 0.981 mg L^{-1}	Tea infusions, green & black tea	[39]
11.GCE/SWCNT-SubPc	Catechin	DPV	0.4 V	3.0[a]	13 nM	Water & real tea samples	[40]
12.GCE/PEP	Gallic acid	AdSV	0.55 V	1.88[a]	0.66 μM	Black tea	[41]
13.GCE/CdSe	Theophylline	DPV	1 V	6.0[b]	0.4 μM	Tea, cola, milk, fruit juice, preserved fruit	[42]
14.GCE/MWCNT-PDDA/Nf	Caffeine	CV	1.2 V	2.5	0.05 μM	Oolong tea	[43]
15.GCE/AuNPs/PDA	Caffeine	DPV	1.30	7.0	0.79 μM	Oolong tea	[44]
16.GCE/rGO/Pt-PEDOT	Caffeic acid	DPV	0.45 V	2.5[b]	0.002 μM	Green tea & Black tea	[45]
17.PEDOT/Co^{2+}-EDTA	Rutin				1.67 nM		[46]
18. GCE/GMC	1,4-DHB 1,2-DHB 1,3-DHB	DPV	0.05 V 0.15 V 0.5 V	7.0[a]	0.91 μM 1.31 μM 0.67 μM		[51]
19. GCE/Chit@GMC	1,2,3-THB 1,2-DHB 1,3-DHB	FIA-DECD	0.1 V 0.7 V	7.0[a]	 1.089 μM 0.892 μM	Black tea, Ginger tea, Green tea, Herbal tea	[52]
20. 6B-PGE	1,2-DHB 1,3-DHB 1,4-DHB	DPV	0.2 V 0.55 V 0.05 V	7.0[a]	0.719 μM 2.469 μM 5.072 μM	Commercial tea samples	[53]
21. PGE	Polyphenol as antioxidant	FIA	+0.5 V +0.8 V	4.0[a]		Several regional teas, green tea, fruit flavored green tea were analyzed as real samples.	[54]

Table 2. continued

CME	Analyte/s	Tech.	Potential	pH	Detection limit	Real samples	Ref.
22. SPCE/PME	Gallic acid	FIA	0.50 V 0.24 V	3.0[a] 7.0	0.076 µM 0.21 µM	Green tea	[55]
23. GCE	Polyphenol as antioxidant	FIA-well-plate	0.2 V	2.82[a]	0.003–0.012 mg L^{-1}	Thailand tea infusions and fruit juices	[56]
24. SPCE	Total antioxidant capacity	Flow mixing system	–0.05 V	6.0[a]		Ascorbic acid, green tea, fruit juices and white wine	[57]
25. GCE	Catechin	BIA-MPA	0.4 V	4.5[a]	0.03 µM		[58]

a = vs Ag/AgCl, b = vs SCE.

current response of the modified electrode, as the tea infusions were added. Recently in 2019, Kulikova et al., introduced polyaniline based CME for the determination of antioxidant property [35]. Polyaniline-DNA-polyphenazine dye modified GCE, designated as GCE/PANI/DNA-PPD, was developed to examine the antioxidant powers of tea samples. The polyaniline was formed over the GCE by potentially cycling in Britton-Robinson (BR) buffer (pH 7.0) with aniline in the solution, which gave a redox response at $E_{1/2} = 0.48$ V. DNA was deposited over the formed polymer, followed by immobilization of phenazine dyes (NR-neutral red; MB-methylene blue; MG-methylene green). The incorporation of DNA over the polyaniline formed, was to stabilize the peak current of polyaniline formed on the glassy carbon electrode in weakly acidic and neutral media. Using the prepared electrode, different tea brands were analyzed. The working medium for the various dyes NR, MB and MG were maintained at BR buffer pH 6.0, 7.0 and 8.0, respectively. From the above analysis, the group summarized that this electrode may be applied for analyzing antioxidant power in food and beverages. Again in 2019, Trofin et al., reported the voltammetric detection of antioxidant capacity using screen-printed microelectrodes (SPME) in tea samples (pH 7.0, ammonium acetate buffer) [36]. They quantified the antioxidant capacity with SPME using cyclic voltammetry versus open circuit potential (CV versus OCP) as well as DPV method and compared them with the spectrophotometric method (CUPRAC with trolox). The results from both the methods were in good agreement with each other.

In literature, several CMEs were developed to detect the total content of catechin in the tea samples (Table 2). In 2014, Devadas et al., had grown yttrium hexacyanoferrate (YHCF) over functionalized multiwalled carbon nanotube (f-MWCNT) modified GCE (GCE/fMWCNT/YHCF), and utilized for the determination of CE in 0.1 M KNO_3 (pH = 6.0) using linear sweep voltammetry (LSV) technique, which gave response at a peak potential of 0.35 V [37]. The CME was further extended to analyze catechins in commercially available green and oolong tea samples. In 2015, Vilian et al., reported the detection of catechin with GCE/fMWCNT/MnO_2/Pt modified electrode [38], in red wine, green and black tea commercial samples using square-wave voltammetry technique (SWV), with $E_p = +0.2$ V, in PBS (pH 6.5). They reported 100 % recovery rate for the catechin in real samples. In 2016, Sen et al., prepared a redox mediator, chloramine-T (CT) modified on three different matrices, namely screen-printed electrode (SPE), GCE, and platinum electrode (Pt), for the determination of catechin in PBS (pH = 6.8) using CV technique [39]. They observed that the redox mediator, CT has mediated polyphenols into quinones by reducing itself to p-toluidine sulfonamide, which is confirmed with the peak obtained at +0.417 V; +0.45 V; +0.414 V on SPE, GCE, and Pt respectively. The electrocatalysis reaction between the redox mediator and polyphenols were supported by UV-Visible spectroscopy. In

further, X-Ray diffraction (XRD) analysis, scanning electron microscope (SEM) and Fourier transform infrared (FTIR) techniques were used to characterize the modified electrode surface. Using amperometric i-t technique, with that potential obtained from cyclic voltammetry technique, green and black tea infusions were analyzed. The total amount of polyphenols was calculated in terms of catechin content. The results were also compared with the HPLC technique.

In 2019, Senocak et al., developed a new CME using SWCNT and sub-phthalocyanins (SubPc) modified GCE (GCE/SWCNT/SubPc), for the detection of catechin using DPV technique in BR buffer (pH = 3) [40]. Black and green teas of Turkish and Indian brands were used as real samples. In 2013, Hamid et al., detected GA content by developing a polyepinephrine modified GCE (GCE/PEP) [41]. The epinephrine was polymerized as polyepinephrine (PEP) using a cyclic voltammetry technique at pH 7.01 PBS. The developed GCE/PEP was analyzed using in-situ UV-Visible spectroscopy and characterized using field emission scanning electron microscope (FES-EM) analysis. Gallic acid was further determined in black tea real samples. In 2012, Yin et al., reported the electrochemical detection of theophylline using cadmium selenide microparticles modified GCE, designated as GCE/CdSe, in PBS (pH 6.0) [42], and extended it in tea and soft drink commercial samples. From 2017–2018, there were four reports available for the detection of caffeic acid, caffeine and rutin with polymer-modified GCE [43–46]. In 2017, Y. Zhang et al., developed poly (diallyldimethylammonium) chloride immobilized MWCNT modified GCE (GCE/MWCNT-PDDA/Nf) [43] and G. Zhang et al., developed polydopamine – gold nanoparticles immobilized GCE for the determination of caffeine [44]. In 2018, Gao et al., reported the development of poly(3,4-ethylene-dioxythiophene) modified GCE (GCE/rGO/Pt-PEDOT) for the detection of caffeic acid using DPV in BR buffer (pH = 2.5) [45]. The CME was physico-chemically characterized using SEM, transmission electron microscope (TEM), Raman, XRD and X-Ray Photoelectron Spectroscopy (XPS). As an extended application, the developed CME was used to analyze caffeic acid content in black and green tea samples. In 2018, Lu et al., developed a CME by doping PEDOT with transition metal-EDTA complex for the determination of rutin in buckwheat tea samples [46]. So far, we have discussed about the electrochemical techniques (Table 2) that were used both for the detection of a single compound or for a mixture of polyphenols using several CMEs and extending the same for the commercially available tea and other food samples. Even, enzymes were also utilized for the electrochemical detection of tea constituents (single compound), which is discussed in the next section.

2.3 Bioelectrochemical Sensing of Tea Polyphenols

In the past twenty years, there are few reports, for the utilization of biomolecules like DNA and enzymes like Tyrosinase (Ty); polyphenol oxidase (PPO), for the development of biosensors for the detection of single constituents of tea (Table 3). In 2004, Ferancova et al., reported the direct detection of antioxidant property in tea extracts using a SPE/DNA/$[Co(phen)_3]^{3+}$ biosensor in pH 7 PBS [47]. The real samples were prepared by immersing the commercially available tea bags in hot water for some time of 5, 3 and 10 minutes for green and black teas, white tea and hyssop, respectively. From the results, it was concluded that the antioxidant activity was maximum for green tea followed by black, white and hyssop tea samples. The temperature of water used to prepare the tea extracts influenced their antioxidant property. As a reference, the analysis was also repeated with DPPH assay. In 2017, Datta et al., developed a new biosensor by using tyrosinase enzyme with gold nanoparticles (AuNPs) [48]. Eggshell membrane (ESM) was used as a base for the deposition. For that, the ESM was peeled out from a freshly broken egg and was washed with an excess quantity of deionized water. Then, it was preserved in pH 6 PBS at a temperature of 4 °C. The obtained membrane was sliced into pieces of about 15 mm diameter in circular shapes and was soaked in a solution of $HAuCl_4$ (2 ml of 0.4 mg/ml-optimized concentration) containing watch glass for about 1.5 hrs. The white color of ESM got changed to light brown, which indicates the AuNPs was successfully deposited over the ESM. The prepared AuNPs/ESM was slightly rinsed with PBS for the removal of excess Au (III) ions from the surface of ESM. Over the AuNPs/ESM, Ty was deposited and used for further analysis.

DPV was the technique that was used for the detection of the tea polyphenols viz., catechin hydrate (CH), GA and caffeic acid (CA) separately. As an extension, the biosensor was used in the detection of polyphenols in tea and wine samples and was compared with the conventional technique (HPLC). In 2017, Soussou et al., reported the determination of tea polyphenols, using Ty enzyme, immobilized over the layered double hydroxide (LDH) hybrid of cobalt and aluminum (designated as CoAl) modified gold SPE (AuSPE) [49]. The CME was designated as AuSPE/CoAl/Ty. The LDH–CoAl was characterized using atomic force microscopy (AFM) studies, with and without the modification of Ty. The CME, thus prepared, showed a good result for the determination of polyphenols in green tea extracts. Recently, in 2019, a biosensor was developed by Zhong et al., based on polyphenol oxidase enzyme for the detection of rutin [50]. The GCE was modified with mesoporous carbon (FDU-15) over which AuNPs were deposited, followed by PPO, designated as GCE/FDU-15/AuNPs/PPO. The developed biosensor was sensitive and selective to rutin in aqueous solution and dark tea

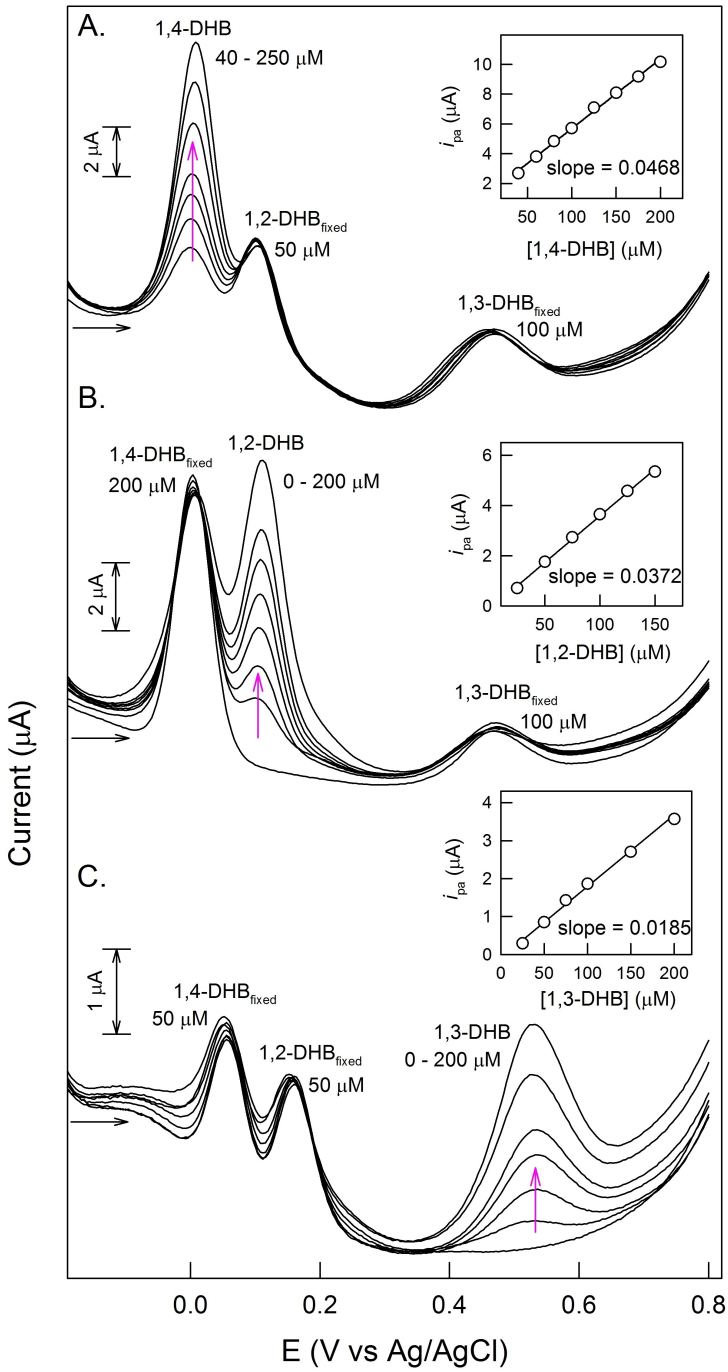


Fig. 1. DPV response of concurrent detection of ortho, meta and para DHB isomers (by varying one isomer concentration at a time), with GCE/GMC modified electrode. Insets: Plot of i_{pa} vs analyte concentration. $E_{amp} = 50$ mV; $E_{step} = 4$ mV; pulse period = 0.5 sec, pulse width = 0.2 sec. Reprinted with permission from the RSC publisher [Ref. No. 51].

samples, which were done using the amperometric technique.

2.4 Simultaneous Electrochemical Detection of Multi-constituents by the Separation-less Method

The techniques mentioned above help in the detection of a total entity present in tea samples. In general, it is a tedious and challenging process to extend those techniques for the detection of two or more substances in a mixture of tea samples. The tea polyphenols consist of ortho and meta DHBs and 1,2,3-THB as functional groups (Scheme 1). They are all intramolecularly connected to one another to form catechins and their derivatives. For instance, CE and EC are made up of o-DHB and m-DHB; EGC and EGCG contain m-DHB and

Table 3. Literature collection of the bioelectrochemical sensors for tea polyphenol analysis.

CME	Analyte	Tech.	E/V vs Ag/AgCl	pH	Real samples	Ref.
1.SPE/DNA/$[Co(phen)_3]^{3+}$	Polyphenols as Antioxidants		0.2 V	7.0	Green, black, white and hyssop teas	[47]
2.ESM/AuNPs/Ty	Catechin hydrate, Gallic acid, Caffeic acid	DPV	0.45 V	6.0	Tea and wines	[48]
3.AuSPE/CoAl/Ty	Polyphenols	CV	0.13 V	7.4	Green tea	[49]
4.GCE/FDU-15/AuNPs/PPO	Rutin	Amp i–t	0.57 V	2.0	Dark tea	[50]

1,2,3-THB and ECG includes all the DHBs and THB (Scheme 1). Our group, in 2012, first initiated the idea for the detection of these functional groups of tea polyphenols. It is nothing but, the simultaneous detection of DHBs, and THB functional groups as a quality assessment for tea. This was done using graphitized mesoporous carbon (GMC) modified over GCE (GCE/GMC) at a neutral pH buffer [51], using DPV technique (Figure 1). The standard o-DHB, m-DHB and p-DHB samples were initially tested for the analysis, by altering the concentration of one analyte at a time. Later, when the CME was extended to the real samples, we faced the real challenge of functional group analysis. This is because the aromatic fused rings are present in tea polyphenols, which makes it difficult for its quantification. Since 1,2,3-THB functional group is present in commercial tea samples, instead of 1,4-DHB derivative (hydroquinone), pyrogallol (1,2,3-THB) was alternatively used as a control sample for comparison with the commercial tea sample responses. The recovery value calculated from the real sample analysis was found to be ~100 %. Since the development of CME was economical and efficient, it can be used for the analysis of functional groups of tea polyphenols without separation (Figure 2).

In 2016, our group assessed the quality of tea by analyzing the functional group of tea polyphenols in neutral pH PBS [52]. Similar to the previous report, GMC modified GCE was used, additionally chitosan was mixed with GMC to form GMC@Chit composite (GCE/GMC@Chit). The prepared electrode was utilized for the detection of functional groups of polyphenols using DPV technique. Such an electrode was found to withstand the strong hydrodynamic condition adopted in the flow injection analysis (FIA) technique (will be discussed later in the next section). The formation of GMC@Chit composite was examined by TEM and Raman spectroscopy. A dark polymer matrix like layer was observed over the agglomerated GMC particles. In order to check the electronic behavior, the CME was analyzed using 5 mM $K_3[Fe(CN)_6]$ in 0.5 M KCl. A sharp and precise redox peak was observed in the case of modified electrode whereas the unmodified electrodes failed to show the redox response (GCE/Chit and GCE/GMC). The comparison of different carbon matrices towards the functional group analytes were also recorded using cyclic voltammetry and DPV techniques. GCE/GMC@Chit was found to show a prominent response over other carbon matrices (MWCNT, carbon nano fiber – CNF, fMWCNT, and graphite nano powder – GNP). Thus, GMC@Chit modified GCE was chosen as the optimal electrode for the analysis of functional group analytes and commercially available real tea samples. Green, black, herbal and ginger flavored tea samples from various parts of India, viz., Bengaluru, Kochi, Cochin, Assam and Jaipur, were collected, and infusions were collected by heating the samples in distilled water for 30 minutes at 80 °C in an oil bath, and further used for analysis. The recovery was found to be ~100 %. In 2018, our group have used the

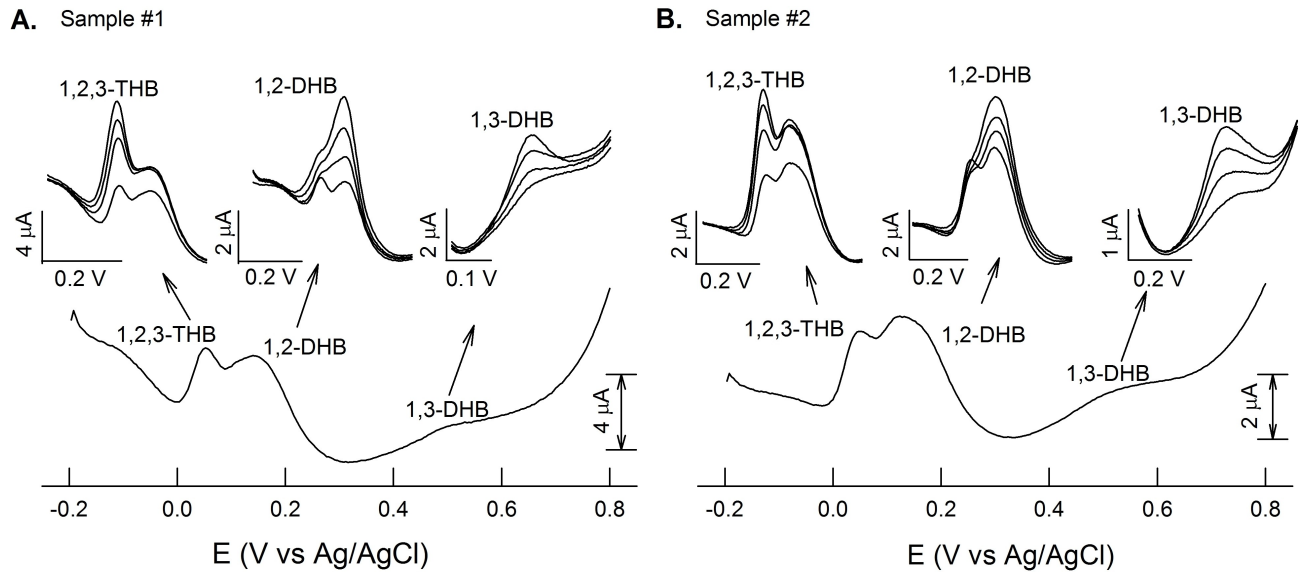


Fig. 2. DPV response curves obtained for real samples extracted from hot water by using GCE/GMC. DPV parameters are as in Figure 1. Reprinted with permission from the RSC publisher [Ref. No. 51].

pre-anodized 6B-PGE (pencil graphite electrode with 6B grade), designated as 6B-PGE*, for the detection of the functional groups of tea polyphenols in a neutral pH PBS (Figure 3) [53]. Previously Buratti et al., utilized it for detection of polyphenols as antioxidant power in tea infusions, which will be discussed in the next section. 6B-PGE* was conceived by potentiostatically polarizing 6B-PGE at $E_{app} = 2$ V (vs Ag/AgCl) for 3 minutes in PBS (pH 7). The pre-anodization of PGE was found to activate functional groups with electron-rich oxygen groups, like phenolic, carbonyl, carboxylic, ether, alcoholic etc. Different grades of pencils were also tested for the detection of functional groups of tea polyphenols (Figure 3). Of all the categories, 6B was found to show the maximum response for 100 µM, 50 µM and 20 µM of o-DHB, m-DHB and p-DHB (1,2,3-THB) respectively. Here too, the CME was extended to two commercially available real samples (Figure 4), whose recovery was found to be ~100 %. Regarding the interference, it is noteworthy that except polyphenols, caffeine and theaflavin, all other contains in tea extract are electro-active in compounds. In general, caffeine and theaflavin get oxidized at potential E_{pa}, ~1.2 V vs Ag/AgCl (pH 7), which is much higher than that of the polyphenols oxidation reaction potentials, 0–0.6 V vs Ag/AgCl [51] and hence, there is no serious interference effect for the tea polyphenol sensing.

2.5 Flow Injection Analysis Coupled Electrochemical Detection of Tea Polyphenols

Similar to HPLC, FIA, is a well-established approach that has been operated without any column for electroanalysis. It involves the discreet injection of an analyte through the injector and electrochemical detector. The unique feature of FIA is that multiple working electrodes can be used at the same time operating at different potentials. It helps in the simultaneous detection of analytes. In 2008, Buratti et al., reported the detection of total polyphenolic content as well as the antioxidant power in tea infusions using flow injection technique (in amperometric mode) utilizing PGE as a detector in pH 4 acetate buffer [54]. The experimental parameters were optimized using caffeic acid as a standard and the optimized PGE was used for analyzing the total phenolic content as well as the antioxidant power of tea samples. The response was compared with the conventional Folin-Ciocalteau and DPPH assay. By analyzing the pencil quality (HB, 2B; 2H, 5H) and surface area (mm diameter) of the PGE, they found that HB with 4 mm diameter showed the maximum response for detecting caffeic acid and was used throughout for other studies. Five commercially available black teas with apple flavor (from Kenya), cherry flavor, Ceylon black tea, Himalayan black tea, Detheinated black tea; peach flavored green tea, green teas in bags and leaves, Japanese green and oolong teas, Chinese red and white tea samples were purchased from the local market and used as real samples. Before the analysis, the tea samples were boiled in water for 4 minutes and cooled to room temperature, 50 mL of the test solution was diluted 100 times with the FIA carrier solution. The technique was economical, renewable with low techie work and was useful during the on-field analysis of polyphenol content. After nearly seven years, in 2015, Su et al., reported a sensitive, selective and direct detection of GA using FIA technique with polymelamine (PME) modified over the screen-printed carbon electrode (pre-anodized SPCE/PME) [55]. The SPCE was pre-anodized at 2 V for 5 minutes in pH 7 PBS. This enables the oxygen-rich centers on SPCE, as mentioned earlier. Melamine was electrochemically polymerized over the

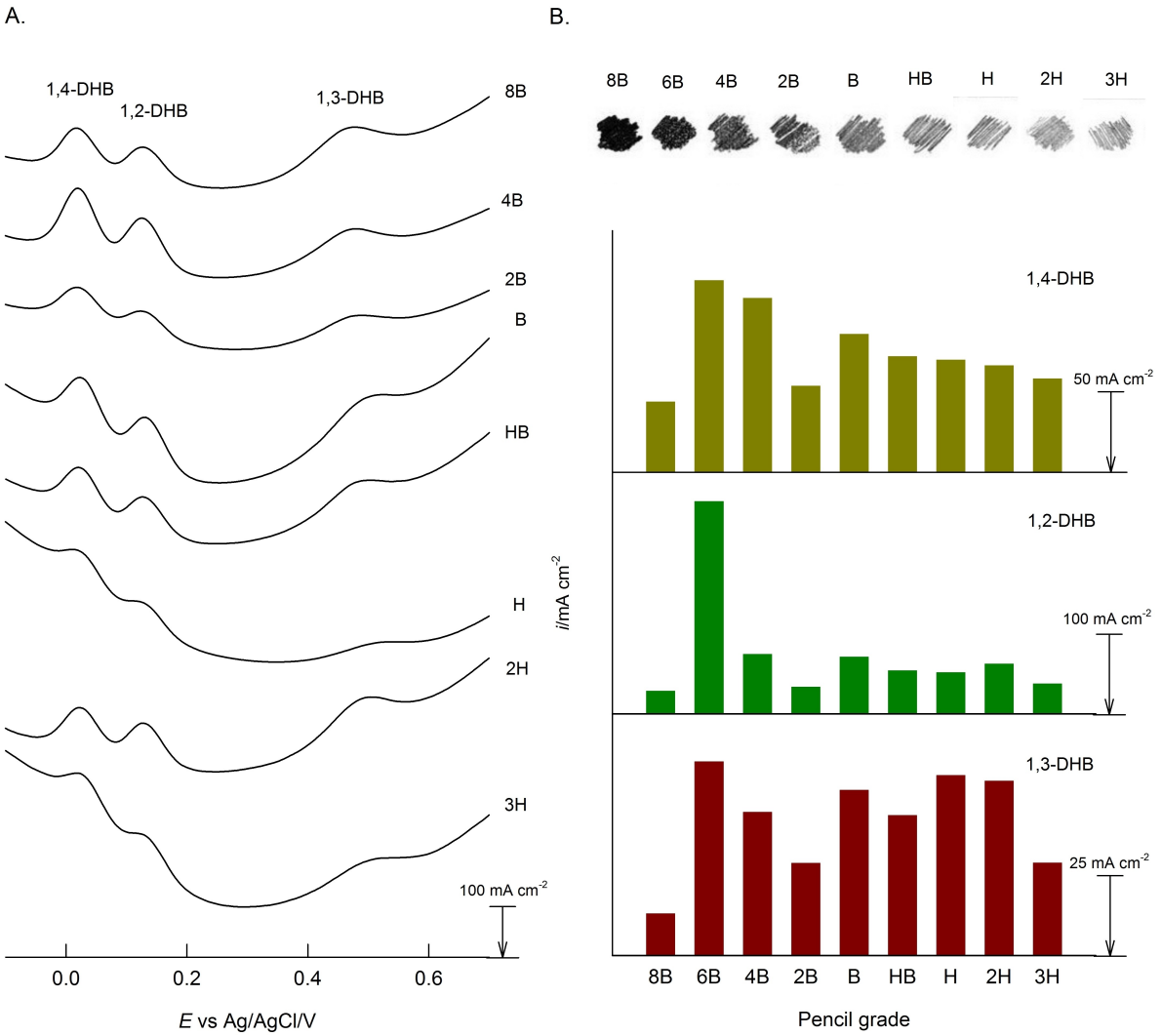


Fig. 3. (A) Comparison of DPV responses for the various PGEs (pre-anodized), 8B, 6B, 4B, 2B, B, HB, H, 2H and 3H for concurrent DHB isomers electrochemically in pH 7 PBS. (B) Comparative plot of i_{pa} of the various DHB isomers used vs different PGE*. Inset: Sketches of various pencil grades. Reprinted with permission from the RSC publisher [Ref. No. 53].

pre-anodized screen-printed carbon electrode (SPCE*) in melamine containing 0.1 M HCl. The modified electrode was characterized using AFM, SEM, FESEM and water contact angle measurement techniques. The modified electrode was used for the direct detection of GA through FIA at two different pHs (pH 3, with $E_{app} = 0.5$ V and pH 7 with $E_{app} = 0.24$ V) PBS. The results obtained from this technique were compared with the Foline-Ciocalteu technique as a reference and the comparison was satisfactory. The newly developed electrode was further extended to two commercially available tea samples and the recovery was found to be ~100 %. The very next year in 2016, our group reported the detection of functional groups of polyphenols present in tea by coupling FIA with a dual electrochemical detector (FIA-DECD) as mentioned in the previous section [52]. The GCE/GMC@Chit was used as the CMEs at different operating potentials (Figures 5 and 6). The flow rate of the carrier solution (pH 7 PBS) was optimized to be 0.8 mL min^{-1} and the E_{app} of the CME was optimized as 0.1 V and 0.7 V for the detection of 1,2,3-THB (case-1) at electrode 1 and a mixture of o-DHB + m-DHB + 1,2,3-THB (case-2) at electrode 2 respectively. The applied potentials optimized in that work are found to be selective to the respective analytes. In case-1, at $E_{app} = 0.1$ V, the 1,2,3-THB, was detected and the concentration was quantified. In case-2, the o-DHB, m-DHB and 1,2,3-THB functional groups present in the mixture were simultaneously identified and the strength of the mixture was determined. From the cases 1 & 2, the concentration of o-DHB and m-DHB functional groups were back-calculated by subtracting the concentration of 1,2,3-THB (in case-1) from the concentration of the mixture (in case-2). As mentioned earlier, different commercially available tea samples from different parts of India were used as real samples for the detection of functional groups of tea polyphenols using

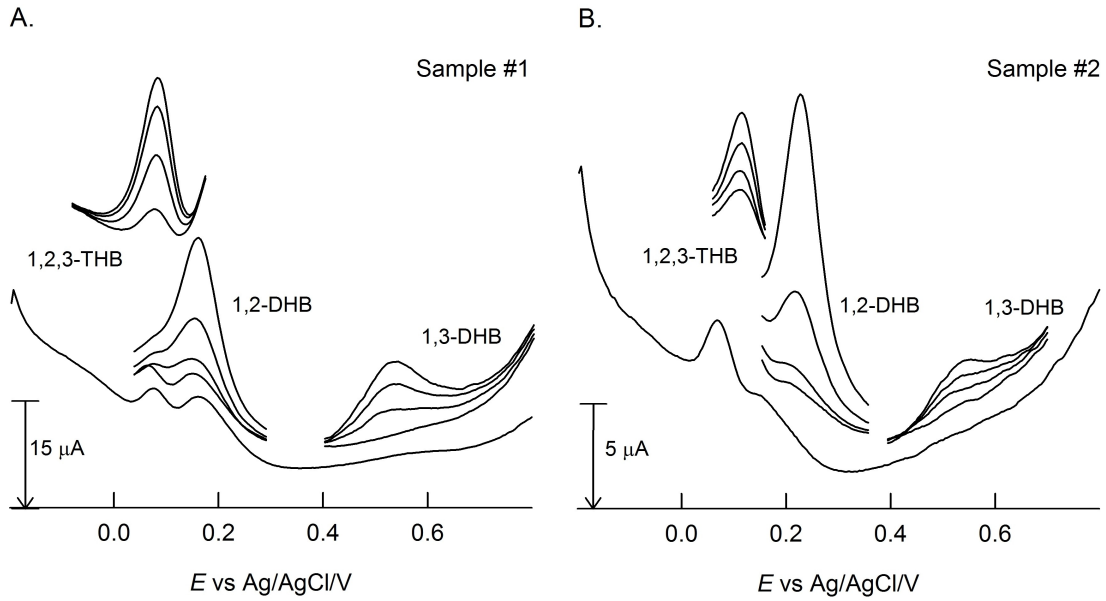


Fig. 4. Compiled DPV response curve of pre-anodized 6B-PGE for detecting the tea polyphenols (o-, m-DHBs and 1,2,3-THB) present in two discrete tea extracts (1 and 2) electrochemically using the approach of standard addition. DPV conditions: same as in the Figure 1. Reprinted with permission from the RSC publisher [Ref. No. 53].

FIA-DECD and the recovery was found to be ~100 %. In 2018, Klayprasert et al., reported the fast screening of the antioxidant capacity, by using flow injection analysis coupled with 96-well-plate [56]. This analysis was based on the reaction between $Cr_2O_7^{2-}$ ion and test antioxidant capacity CHROMAC assay. The antioxidants and dichromate react slowly and steadily in the 96-well-plate, which leads to the decrease in standard dichromate ion concentration, which in turn reacts with iodide to form triiodide. After the reaction, the decrement in the $Cr_2O_7^{2-}$ ion was quantitatively determined by FIA technique in the presence of iodide (I^-) in an acid medium as a triiodide on GCE at 0.2 V vs Ag/AgCl. The electric current signal was inversely proportional to the antioxidant content. This method was used to determine the total antioxidant capacity in tea and herbal extracts, fruit juices. In 2018, Veenuttranon and Thai Nguyen reported the determination of antioxidant capacity by a programmable flow injection analysis system in a couple with electrochemical DPPH and screen-printed carbon electrode (observed a redox signal at $E^{\circ\prime}$ ~0.05 V vs Ag/AgCl in ethanol-PBS) [57]. The results obtained were validated with the traditional spectrophotometric method. This method was used to calculate the total antioxidant capacities of ascorbic acid as a standard and some selected samples like fruit juices, white wine, and green tea. The group concluded that the above method can be used to evaluate the antioxidant capacity in food and biological samples. In 2018, Ribeiro et al., reported the determination of CE using coupled batch injection analysis with multiple pulse amperometric technique [58]. The unmodified GCE was used as a working electrode at a pH 4.5 of acetate buffer. To avoid the passivation by the oxidized CE, the electrode was given three potentials, viz., +0.4 V as oxidation potential, 0.0 V as conditioning potential and +1.4 V as cleaning potential, thus leading to the quantification of CE present in samples. This method was used to quantify the CE content in real samples. Table 4 summarizes the list of various abbreviations used in this work.

3 Conclusions and Future Prospective

In this article, we have summarized the different electrochemical techniques available for the detection of tea polyphenols. Conventionally, HPLC coupled electrochemical detectors were used to determine the catechins, quercetin and other derivatives as an antioxidant capacity and tea infusions. The obtained results were compared with the standard procedures like DPPH and FRAP. Although the usual separation process provides a benchmarking analysis of tea polyphenols, the tedious and time-consuming procedures limit this assay for routine analysis. For instance, in general, hundreds of tea samples are received per day in the tea industry-quality control systems and it is challenging to complete the analysis part within a short time of the test-samples. On the other hand, providing total polyphenols content along with quantification of gallate-group (1,2,3-dihydroxy benzene derivative) can fulfill the data for the tea-industry quality control requirement. In this respect, direct electrochemical detection of tea constituents as a single voltammetric signal is highly recommended. Comparing with the separation techniques, electrochemical detection is found to be a very effective, economic, sensitive, selective and rapid analysis for the detection of total tea polyphenol contents. In this respect, bio-electrochemical detection of

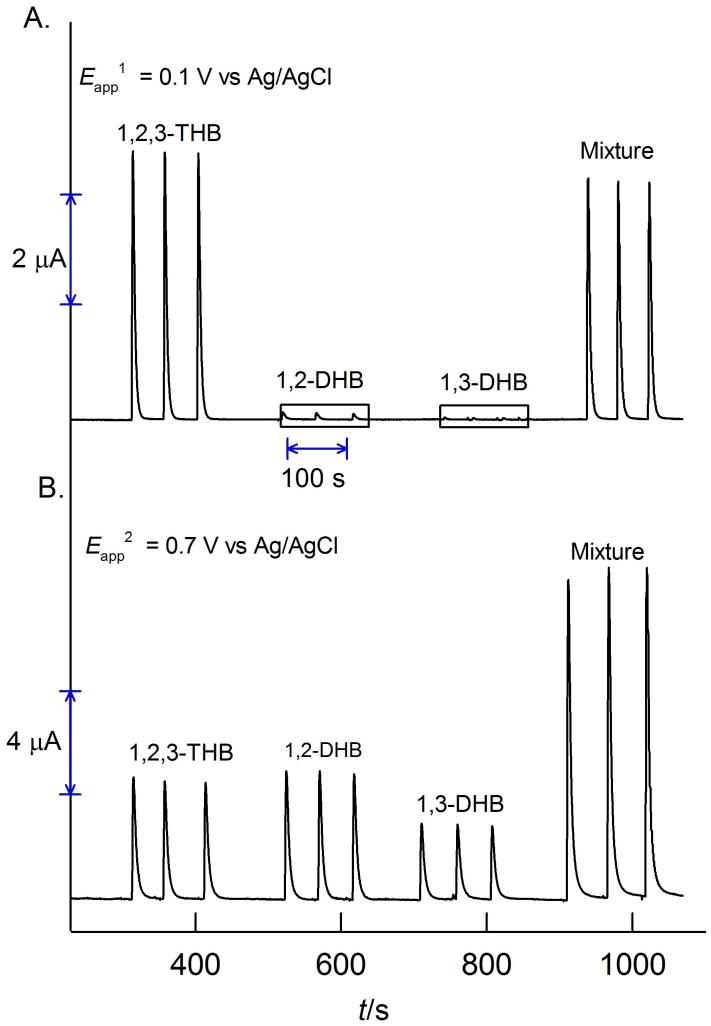


Fig. 5. Flow injection analysis response curves of various polyphenols (100 μM) electrochemically with GMC@Chit modified GCE been operated at (A) E_{app} = 0.1 V and (B) E_{app} = 0.7 V vs Ag/AgCl. Mobile system = PBS (pH 7). Hydrodynamic flow rate = 0.8 mL min^{-1}. Reprinted with permission from the Elsevier publisher [Ref. No. 52].

tea constituents has been carried out using biomolecules like DNA and enzymes like tyrosinase and polyphenol oxidase.Nevertheless, high cost and less-stability factors limit the biomolecular assays for further routine analysis. As an alternate technique, direct and simultaneous electroanalytical sensing of tea polyphenol functional groups, like ortho, meta-dihydroxybenzene and 1,2,3-trihydroxybenzene (gallate group) derivatives, as three voltammetric signals, was introduced as an effective way to check the total polyphenol content and gallate-group. In this connection, coupling flow injection analysis with a dual electrochemical detector, wherein, two fixed applied potentials to detect the mixture of tea samples was reported. In consideration with a quick estimation of the total content of polyphenols along with gallate-group concentration, the above mentioned separation-less electroanalytical method is best-suited one for the routine analysis. In fact, such a methodology will provide automation of the electro-analysis as well. Indeed, single-shot tea polyphenol content measurement gazette similar to the blood sugar estimation tool, which is ordinarily available in the pharmaceutical drug store, is highly necessary. An interdisciplinary approach with a combination of electrochemistry and mechatronic research experts are required to successfully develop such a tea polyphenol sensing gazette. We hope in the near time, a cellphone-based detector in combination with the disposable or reusable type of tea polyphenol sensor will be developed to support not only for tea industry but also for the general public who wish to drink the quality tea products.

Acknowledgements

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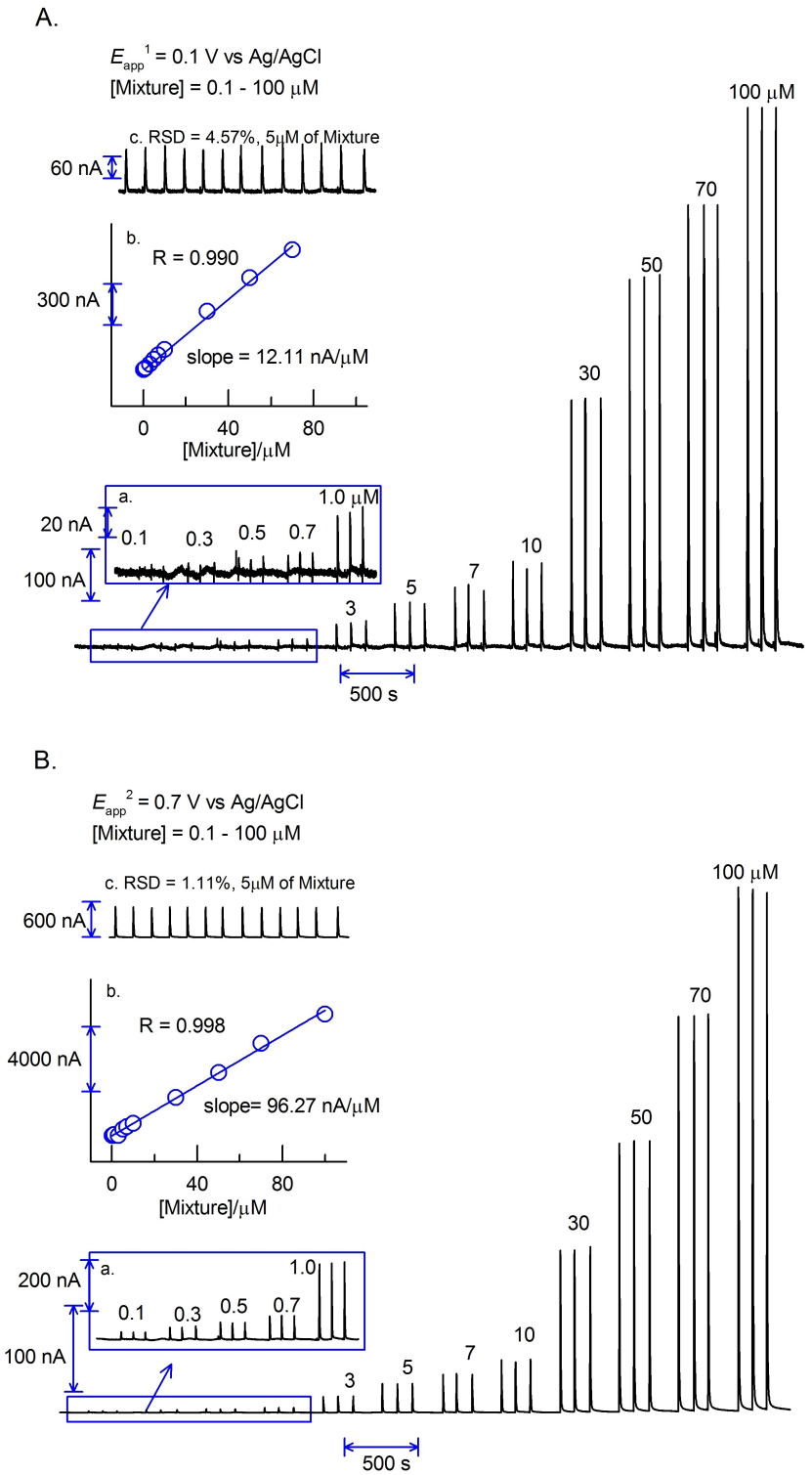

Fig. 6. FIA-DECD response curves of a mixture of o-DHB, m-DHB and 1,2,3-THBs operated simultaneously at (A) E_{app}^{1} = 0.1 V and (B) E_{app}^{2} = 0.7 V vs Ag/AgCl at a concentration of 0.1 to 100 μM with a dual GMC@Chit modified GCE-ECD. Mobile system = PBS (pH 7), hydrodynamic flow rate = 0.8 mL min^{-1}. Inset: (a) amplified image of the response at low concentration, (b) I vs. [analyte] and (c) thirteen consecutive spikes of 5 μM of the mixture solution at their corresponding E_{app}. Reprinted with permission from the Elsevier publisher [Ref. No. 52].

Table 4. List of abbreviations used in this work.

S.No.	Abbreviations	Acronyms
1.	1,2,3-trihydroxybenzene	1,2,3-THB
2.	1,2-dihydroxybenzene	1,2-DHB or o-DHB
3.	1,3-dihydroxybenzene	1,3-DHB or m-DHB
4.	2,2′-azinobis(3-ethylbenzothiaziline-6-sulfonate	ABTS
5.	2,2-diphenyl-1-picrylhydrazyl	DPPH
6.	Atomic force microscopy	AFM
7.	Britton-Robinson	BR
8.	Cadmium selenide	CdSe
9.	Caffeic acid	CA
10.	Carbon nano fiber	CNF
11.	Carbon paste electrode	CPE
12.	Catechin gallate	CG
13.	Catechin hydrate	CH
14.	Catechins	CE
15.	Chemically modified electrode	CME
16.	Chitosan	Chit
17.	Chloramine-T	CT
18.	Cyclic voltammetry	CV
19.	Deoxy ribonucleic acid	DNA
20.	Differential pulse voltammetry	DPV
21.	Dual electrochemical detector	DECD
22.	Egg shell membrane	ESM
23.	Electrochemical detector	ECD
24.	Epicatechin	EC
25.	Epicatechin-3-gallate	ECG
26.	Epigallo catechin	EGC
27.	Epigallocatechin-3-gallate	EGCG
28.	Ferric reducing antioxidant power	FRAP
29.	Field emission scanning electron microscope	FESEM
30.	Flow injection analysis	FIA
31.	Fourier transform infra-red	FTIR
32.	Functionalized multiwalled carbon nanotube	f-MWCNT
33.	Gallic acid	GA
34.	Gallocatechin	GC
35.	Gallocatechin gallate	GCG
36.	Glassy carbon electrode	GCE
37.	Gold nanoparticles	AuNPs
38.	Gold SPE	AuSPE
39.	Graphite nano powder	GNP
40.	Graphitized mesoporous carbon	GMC
41.	High pressure liquid chromatography	HPLC
42.	Layered double hydroxide	LDH
43.	Linear sweep voltammetry	LSV
44.	Manganese oxide	MnO_2
45.	Methylene blue	MB
46.	Methylene green	MG
47.	Multiwalled carbon nanotubes	MWCNT
48.	Nafion	Nf
49.	Neutral red	NR
50.	Octadecyl silica	ODS
51.	Open circuit potential	OCP
52.	Pencil graphite electrode	PGE
53.	Pencil graphite electrode – pre-anodized	PGE*
54.	Phosphate buffer solution	PBS
55.	Platinum electrode	Pt
56.	Poly(3,4-ethylenedioxithiophene)	PEDOT
57.	Poly(diallyldimethylammonium chloride)	PDDA
58.	Polyaniline	PANI
59.	Polydopamine	PDA
60.	Polyepinephrine	PEP
61.	Polymelamine	PME
62.	Polyphenol oxidase	PPO

Table 4. continued

S.No.	Abbreviations	Acronyms
63.	Polyquercetin	PQ
64.	Reactive oxygen species	ROS
65.	Reduced graphene oxide	rGO
66.	Scanning electron microscope	SEM
67.	Screen printed carbon electrode	SPCE
68.	Screen printed carbon electrode – pre-anodized	SPCE*
69.	Screen printed electrode	SPE
70.	Screen-printed micro electrodes	SPME
71.	Square-wave voltammetry	SWV
72.	Subphthalocyanins	SubPc
73.	Transmission electron microscope	TEM
74.	Tyrosinase	Ty
75.	X-Ray diffraction	XRD
76.	X-Ray Photoelectron Spectroscopy	XPS
77.	Yttrium hexacyanoferrate	YHCF

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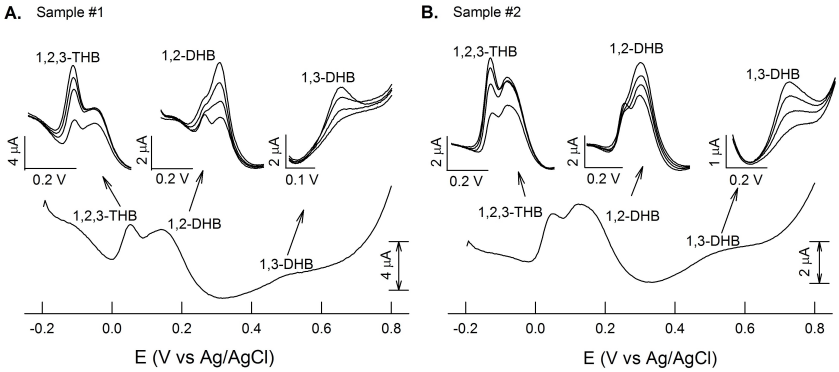

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