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Tea quality assessment by analyzing key polyphenolic functional groups using flow injection analysis coupled with a dual electrochemical detector

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ABSTRACT

Tea, one of the most consumed beverages in the world, has several health benefits which include antioxidant and reducing the risk of diabetes, heart-attack and cancer etc. Polyphenols such as catechin, epicatechin, epicatechin gallate, epigallocatachin and epigallocatechin gallate (EGCG), which generally contain combination of 1,2-dihydroxy benzene (1,2-DHB), 1,3-dihydroxy benzene (1,2-DHB) and 1,2,4-trihydroxy benzene (1,2,3-THB) functional groups are rich in green tea. Among the various polyphenols, EGCG (1,2,3-trihydroxybenzene functional group), is viewed as the most active component for the health benefits and hence it has been assayed in the tea quality assessment. Here in, we report a simple, rapid and separation-less electro-analytical technique based on a flow injection analysis coupled dual electrochemical detector system, in which graphitized mesoporous/Chitosan modified glassy carbon electrodes (GCE/Chit@GMC) set at two different applied potentials (E_{app}), 0.1 (case-I) and 0.7 V vs Ag/AgCl (case-II), controlled by a bipotentiostat, with pH 7.0 phosphate buffer as a carrier solution has been reported for the selective and simultaneous detection of 1,2,3-THB and {1,2,3-THB + 1,2-DHB + 1,3-DHB} contents in tea samples.

1. Introduction

Tea, one of the most important beverages in the world for long time, is an infusion of the leaves of the *Camellia sinensis* plant. Green tea has been used in traditional Chinese and Indian medicine for several health benefits including controlling bleeding, healing wounds, aid digestion, improve heart and mental and health regulate body temperature etc [1,2]. Recent studies have shown green tea has positive effects on everything from weight loss to liver disorders to anticancer activity [3–7]. Studies have also shown the positive impacts of green tea on breast, bladder, ovarian, colorectal, esophageal, lung, prostate, skin and stomach cancers [3–7]. Researchers believe that it is the high level of polyphenols in tea that helps to kill cancerous cells and stop them from proliferation. However, the exact mechanism by which tea interacts with cancerous cells is unknown. In general, the natural tea samples have following types of polyphenolic compounds (~300 mg per cup of tea): catechin (C), (−)-epigallocatechin-3-gallate (EGCG), (−)-epigallocatechin (EGC), (−)-epicatechin-3-gallate (ECG) and epicatechin (EC) (Scheme 1) [1]. It is noteworthy that all these catechin derivatives have a combination of 1,2-diydroxy (1,2-DHB), 1,3-dihydroxy (1,3-DHB) and 1,2,3-trihydroxy benzene (1,2,3-THB) functional groups (Scheme 1). It has been identified that 1,2,3-THB functional groups containing catechin derivative, i.e., EGCG, is a potent compound responsible for the bioactivity of tea [4,8–11]. Depending on the soil nature, regional ecology and post chemical treatment methods, the content of the polyphenols are varied which, it may intern lead to different antioxidant, biochemical and medicinal properties [12,13]. Strong antioxidant potential of these polyphenols was thought to mediate most of the beneficial effects of tea [14,15]. Thus simple and selective method for the quantification of the key ingredients in tea sample is of potential importance in agricultural and food chemistry research.

Despite of several analytical techniques such as high performance liquid chromatography (HPLC) coupled with UV–vis [15,16], spectrophotometry [17], electro-chemiluminescence [18], gas chromatography/mass spectrometry [19], capillary electrochromatography [20], pH-based-flow injection analysis [21] and electrochemical techniques [22–33] developed for tea quality testing in terms of polyphenols content analysis, a conventional method, in which testing the smell and taste of the tea extract by skilled human has been considered to be general protocol in many

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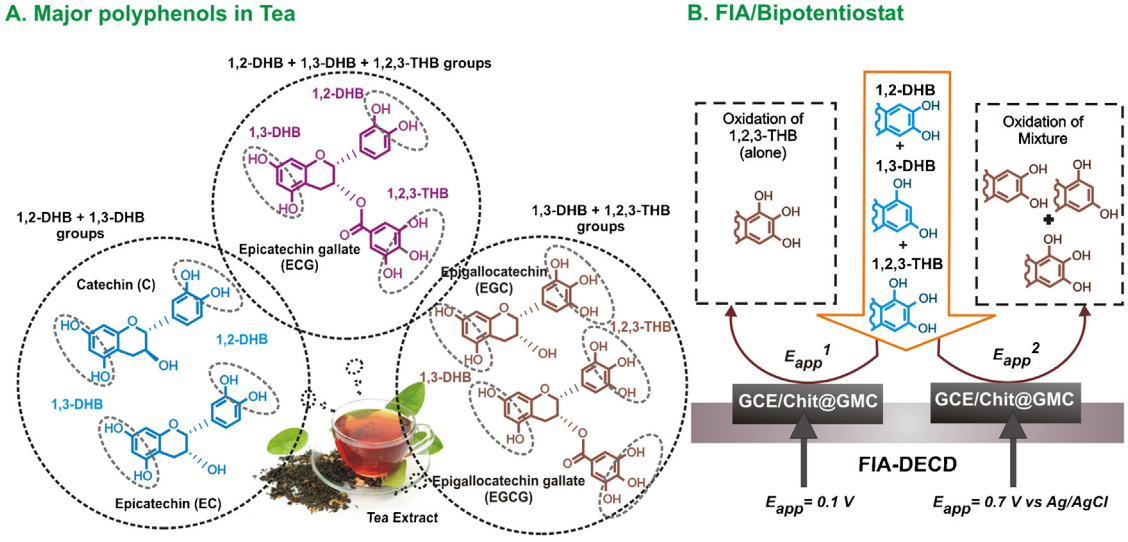
tea industries [34–36]. Note that the reproducibility of the quality scores is limited by mental taste, fatigue and olfactory-adaptation of tasters. Meanwhile, there are few direct electrochemical and bio-electrochemical methods, in which electrochemical oxidation of 1,2,3-THB-functional group, reported in the literature [37–44]. For instance, Singh et al. reported vertically aligned ZnO–PANI nanohybrid film modified Indium-tin-oxide (ITO) electrode for sensing of tea polyphenols [37], especially catechin, where there was a poor redox peak observed for the analyte (EGCG). Alternately, our group developed a meso-porous carbon modified glassy carbon electrode based cyclic voltammetric technique for sensing of tea polyphenols in aqueous solution [27], in which different polyphenolic functional groups such as 1,2-DHB, 1,3-DHB and 1,2,3-THB derivatives of catechin molecules were simultaneously detected. Unfortunately, the reported voltammetric approaches were not viable for practical and routine detection of tea samples analysis. For instance, analysis of low concentration of tea polyphenols in real samples by spiking into 10 mL of the test electrochemical cell (resulted into highly diluted real sample solution) is difficult in the voltammetric detection technique. Herein, we report a new protocol for simple, rapid and separation-less flow injection analysis technique using a dual electrochemical detector (FIA-DECD) consisting of two graphitized mesoporous carbon (GMC)-chitosan chemically modified glassy carbon electrodes (FIA-GCE/Chit@GMC) coupled with a bipotentiostatic system for selective detection of tea polyphenol contents. Note that FIA offers simple detection of analytes at low sample volume (~20 μL), which is quite suitable for the routine analytical application. To the best of our knowledge, a FIA-ECD based analytical technique is never reported for tea polyphenol detection. In this work, a FIA-DECD method for the detection of contents of 1,2,3-THB and [1,2,3-THB + 1,2-DHB + 1,3-DHB]-polyphenolic functional groups discreetly at two different discreet applied potentials, 0.1 and 0.7 V vs Ag/AgCl without any separation technique was demonstrated. This analytical approach was further validated by testing the polyphenols contents in various tea samples with nearly 100% recovery value.

2. Experimental

2.1. Reagents and materials

Graphitized mesoporous carbon materials (50 nm; ~99.95% purity on trace metal basis), multiwalled carbon nanotube (MWCNT, outer diameter: 10–15 nm; inner diameter: 2–6 nm; length 0.1–10 mm and ~90% purity on carbon basis), carbon nanofibre (CNF; ~99.9% purity on carbon basis), graphitized nano powder (GNP; 98% purity), chitosan, CH_3COOH (5%), 1,2-DHB, 1,3-DHB of analytical grade were all purchased from Sigma-Aldrich and used as received without any further purification. 1,2,3-THB was purchased from Sd fine chem. Ltd., India. Aqueous solutions were prepared



Scheme 1. Illustration for the (A) chemical structures of major tea polyphenols derived from dihydroxybenzene (DHB) and trihydroxybenzene (THB) derivatives and (B) flow injection analysis-coupled with dual electrode system (FIA-DECD) for simultaneous detection of 1,2-DHB, 1,3-DHB & 1,2,3-THB functional groups at two different applied potentials, $E_{app}{}^1$ and $E_{app}{}^2$. Amount of [1,2-DHB + 1,3-DHB] was calculated from the current difference between $i_{0.1V}$ and $i_{0.7V}$.

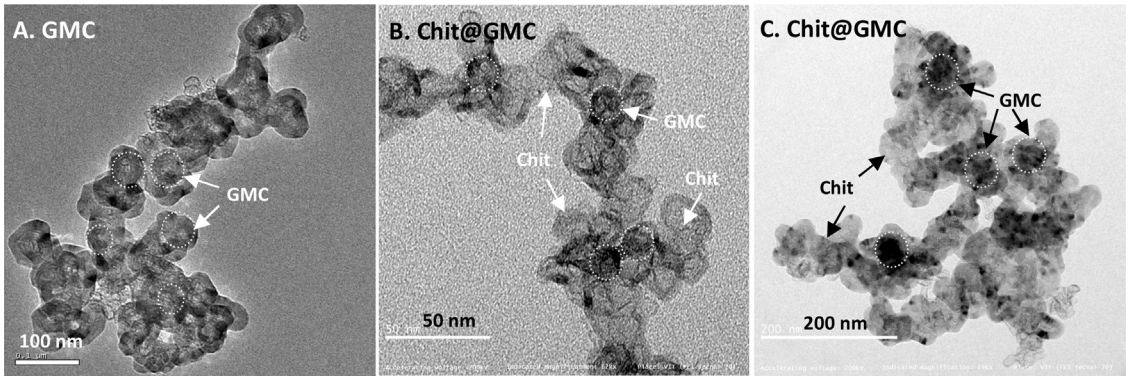


Fig. 1. TEM images of GMC (A) and Chit@GMC (B&C).