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Polyphenol Analysis in Black Tea with a Carbon Nanotube Electrode

Satoshi MURAKAMI,* Shota TAKAHASHI,* Hitoshi MUGURUMA,*† Naomi OSAKABE, Hitoshi INOUE,*** and Tatsuya OHSAWA*****

**Graduate School of Engineering and Science, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto, Tokyo 135-8548, Japan*
***Department of Bioscience and Engineering, College of Systems Engineering and Science, Shibaura Institute of Technology, 307 Fukasaku, Minuma, Saitama 337-8570, Japan*
****Nippon Shizai Co., Ltd., 1-5-6 Bakurou-machi, Chuo, Osaka 541-0059, Japan*

An electrochemical analysis of polyphenols (theaflavin (TF1), theaflavin-3-gallate (TF2A), theaflavin-3′-gallate (TF2B), theaflavin-3,3′-digallate (TF3), and epigallocatechingallate (EGCG)) in a black tea infusion is demonstrated. The characterization of each polyphenol in a solution containing only a single type of polyphenol for a redox reaction at the CNT electrode with cyclic voltammetry (CV) was conducted. The oxidation peak at around +0.30 V for TF1 is assigned to catechol group in a benzotropolone ring. The oxidation peak at around +0.35 V for TF2A, TF2B, and TF3 is assigned to both of the catechol groups in the benzotropolone ring and the pyrogallol group in the gallate ring. The oxidation peak at around +0.35 V for EGCG is assigned to a pyrogallol group in the gallate ring. Current changes of those individual polyphenols at the peak potential are proportional to their concentrations (linear range 0.28 – 94 μM; detection limit 0.11 μM). The CV curve for real black tea, which is mainly composed of a mixture of the mentioned five compounds, is produced by the sum of those. The current change of the mixture solution of polyphenols is also proportional to the mass concentration of the total polyphenols and the sensitivity defined as the slope of current *vs.* concentration plot is independent of the ratio of the individual polyphenols. This indicates that the peak current at around +0.35 V can quantify the total amount of polyphenols in a black tea. Additionally, the shape of the CV curve can roughly estimate the ratio of [catechins]/[theaflavins]. The values for real samples determined from CVs show good agreement with that obtained by high-performance liquid chromatography.

Keywords Carbon nanotube, cyclic voltammetry, theaflavin, epigallocatechin gallate, redox reaction

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Introduction

Black tea is the most popular beverage and represents 78% of all tea production. A black tea is an infusion from fermented leaves of the *Camellia sinensis* plant, whereas a green tea is that from fresh leave without fermentation. The main ingredients of polyphenol in a green tea are catechins, whereas those in a black tea are theaflavins, which is obtained by chemical reactions from catechins. The chemical structure of the four major theaflavins (theaflavin (TF1), theaflavin-3-gallate (TF2A), theaflavin-3′-gallate (TF2B), and theaflavin-3,3′-digallate (TF3)) are shown in Fig. 1. Catechins are also polyphenol of black tea because whole catechins do not change to theaflavin. The chemical structure of major catechin epigallocatechingallate (EGCG) is also shown in Fig. 1. The intake of theaflavin[1,2] as well as catechin[3,4] has healthy benefits, for example, the reduction of cardiovascular and chronic diseases. Therefore, analyses of the amount of total polyphenols are useful for the quality control of food and nutrition indications.

† To whom correspondence should be addressed.
E-mail: muguruma@shibaura-it.ac.jp

The present technique used for polyphenol analysis is high-performance liquid chromatography (HPLC).[5-8] However, HPLC requires pretreatments of the sample, space, solvent, and time, which correspond to increased cost. Spectroscopic methods, such as Folin–Ciocalteu, oxygen radical absorbance capacity, 2,2-diphenyl-1-picrylhydrazyl, and fluorescence recovery after photobleaching also involve the same situation and those are often used as a detection method for HPLC. Thus, the electrochemical analysis of polyphenol in a black tea involves many advantages in terms of a simple operation procedure, low cost of the required equipment, high speed, and portability of the measurement system. There have been many reports concerning the electrochemical determination of polyphenols (catechins) in green teas.[9-17] In contrast, quantitative analysis for polyphenols (catechins and theaflavins) in a black tea has not been done. There are a few report concerning qualitative analysis[18-21] and poor sensitivity at high applied potential (*ca.* 1 V *vs.* SCE).[22] The reason is probably that polyphenols in a green tea are almost dominated by catechins, whereas those in a black tea are mainly composed by a mixture of theaflavins and catechins.[5-8] Carbon nanotube (CNT) electrodes[23] have traditionally been used for catechin detection.[15-17] Therefore, the CNT electrode for theaflavin

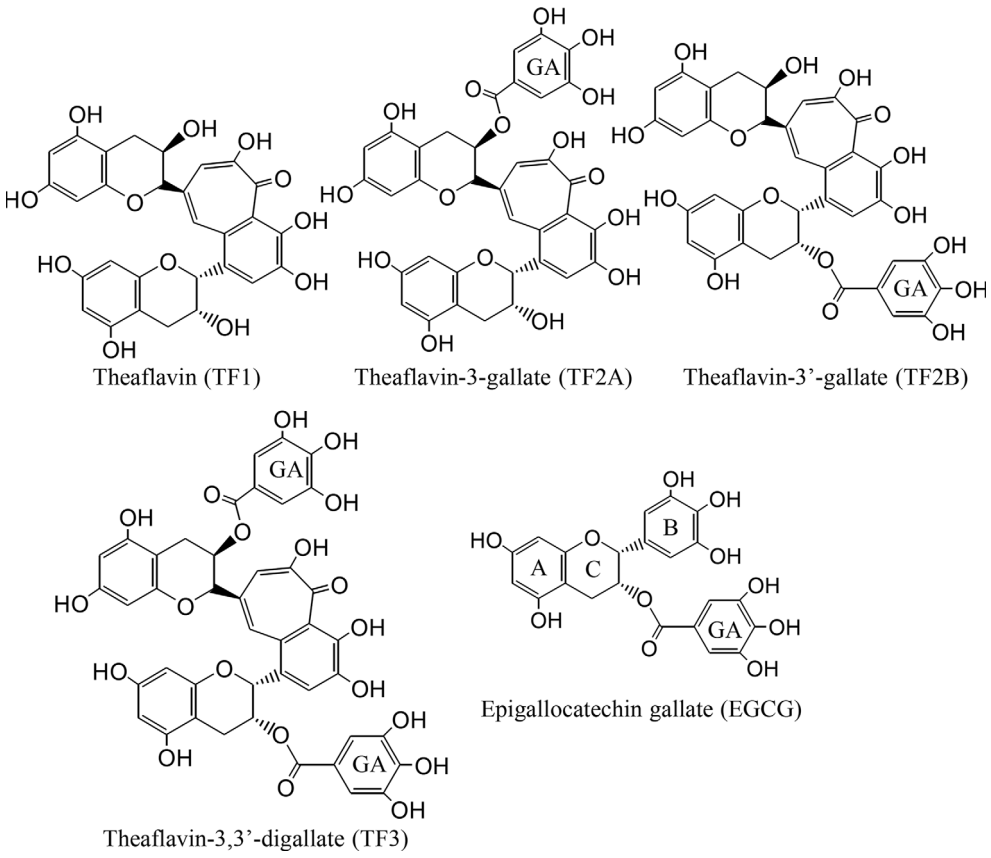

Fig. 1 Molecular structures of polyphenols of a black tea.

detection is thought to be promising in terms of highly electrochemical functionality, such as catalytic effects and a reduction of the oxidation potential. However, it has not been done concerning theaflavin detection with CNT electrodes.

In this report, firstly, the characterization of each theaflavin in a solution containing only a single type of theaflavin for the redox reaction at the CNT electrode is described. Secondly, the quantification of polyphenols in a mixture solution containing multiple theaflavins and catechin is considered. Finally, quantification of the total polyphenols in real black tea samples is mentioned, and the result is compared to values obtained by HPLC. This is the first report concerning the electrochemical quantification of polyphenols featuring theaflavin in a black tea. We demonstrate the quantification of the total polyphenol in the concentration range of 5 – 94 μM and the theaflavin/catechin ratio in black tea with the CNT electrode for the first time.

Experimental

Reagents

TF1, TF2A, TF2B, and TF3 were purchased from PhytoLab (Vestenbergsgreuth, Germany). EGCG was purchased from Nagara Science Co. (Gifu, Japan). Citric acid buffer solutions were purchased from Wako (Osaka, Japan). Multi-walled CNT (4 – 12 layers, length 200 μm) was produced by Taiyo Nippon Sanso Corporation (Tokyo, Japan).

Electrode preparation

The electrode was formed on a screen-printed carbon paste on a plastic substrate. The area of the opening for the working electrode was 9 mm^2. The details can be found in the literature.[24] In brief, an ULVAC (Tokyo, Japan) VEP-1000 plasma generator was used to deposit a 2-nm-thick acetonitrile plasma-polymerized film (PPF)[25] layer onto carbon. The CNT 0.1% w/v was dispersed in water with 0.5% w/v water-soluble cellulose (nonionic surfactant, average molecular weight: 40 kDa). The CNT solution was dropped onto the PPF surface and dried at room temperature for 1 h. Subsequently, the surface was coated with a 6-nm-thick acetonitrile PPF layer.

Measurement

Electrochemical measurements were performed with an electrochemical analyzer (ALS Instruments, 701A West Lafayette, IN, USA) using a three-electrode configuration. Reference (Ag/AgCl saturated KCl, RE-1C) and counter (platinum wire) electrodes were purchased from BAS Inc. (Tokyo, Japan). Since polyphenols are generally fragile at the base, they are prepared and measured at pH 5.3. The solutions were used immediately after preparation and were not stored. Electrochemical measurements were conducted in a 5-mL vessel at 20°C using a citric acid buffer (50 mM, pH 5.3) as the supporting electrolyte, to which stock polyphenol solutions of 0.2 mM were successively added to prepare samples with designated concentrations. The HPLC system (Shimadzu LC-20AD. Kyoto, Japan) consisted of a quaternary pump, a vacuum degasser, an automated sample injector, a column oven, a system controller, and a diode array UV detector set. The separation column was a reversed-phase column (6.0 mm diameter, 150 mm long, YMC-Pack ODS-A, Kyoto, Japan) and 5 μm nominal particle size. The mobile phase was a 19.5% acetonitrile 0.1% formic acid solution for theaflavins and a 20% methanol

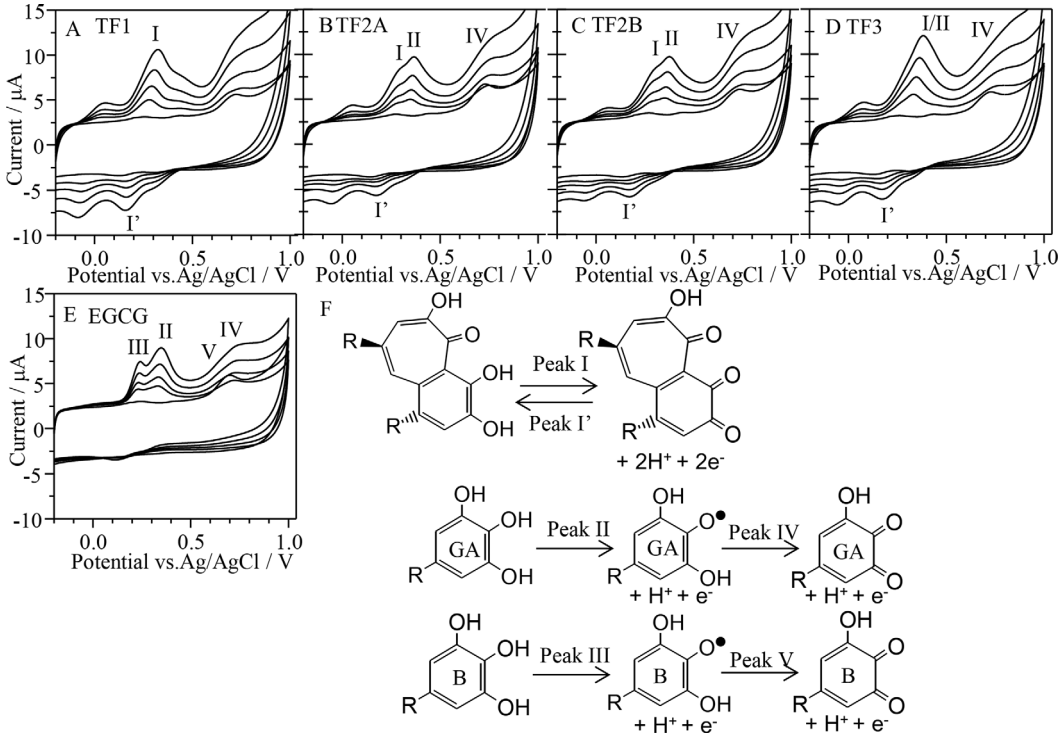

Fig. 2 CVs and peak assignments for (A) TF1, (B) TF2A, (C) TF2B, (D) TF3, and (E) EGCG on CNT electrodes. The concentrations are 0, 22, 39, 65, and 94 μM. The electrolyte used was in 50 mM pH 5.3 citric acid buffer solution. The scan rate was 0.05 V s^{-1}. (F) Electrochemical oxidation route.

20 mM pH 3.0 phosphate buffer solution for catechins. The flow rate was 1.0 mL min^{-1}, the injection volume was 1.0 μL, and the column temperature was 40°C.

Results and Discussion

Characterization of redox reaction of each theaflavins at the CNT electrode

The characterization of each theaflavin for the redox reaction at the CNT electrode was conducted using cyclic voltammetry (CV). The CVs and peak assignments of the electrochemical response toward each theaflavin, TF1, TF2A, TF2B, TF3, and EGCG, at the CNT electrode are shown in Figs. 2A – 2E. The theaflavins-dependent current are observed at the CNT electrode. The reaction scheme is shown in Fig. 2F.

In the anodic scan of TF1 (Fig. 2A), the peak at potential (E_a = +0.32 V) is assigned to oxidation of the catechol group on the benzotropolone ring to quinone (defined as Peak I). This peak is observed at all theaflavins. In the cathodic scan of TF1, one peak at E_c = +0.21 V is assigned to the reduction of quinone back to the catechol group (defined as Peak I′). The ratio of the cathodic-to-anodic current (I_c/I_a) is 0.76, which indicates that the redox reaction of the catechol group is semi-reversible. The small peak pair at around +0.04 and –0.05 V is assigned to a redox reaction of the single hydroxyl group on the benzotropolone ring to quinone (defined as Peak VI and VI′).[26,27]

In an anodic scan of TF2A (Fig. 2B), the peak at the potential (E_a = +0.38 V) is assigned to oxidation of the pyrogallol group on the gallate to the semiquinone radical (defined as Peak II).[28] The shoulder at around +0.32 – 0.35 V is assigned to oxidation of the catechol group on the benzotropolone ring to quinone (Peak I). Therefore, the peak around at +0.38 V for TF2A is due to multiple origins, and those peak positions are too close to be discriminated. This peak is defined as Peak I/II. In the cathodic scan of TF1, one peak at E_c = +0.21 V is assigned to the reduction of quinone back to the catechol group (defined as Peak I′), not due to the pyrogallol group, because the oxidation of the pyrogallol group is irreversible. This is supported by the fact that the ratio of the cathodic-to-anodic current (I_c/I_a) is 0.66. The barely discernible peak at a higher potential (E_a = +0.74 V) is assigned to a further oxidation of the semiquinone radical to the quinone form on the gallate group (Peak IV).[28] The small peak pair at the potential (E_a = +0.037 V) is observed. Possible assignment is the oxidation of the single hydroxyl group on the benzotropolone ring and the subsequent redox reaction of the catechol group of the B-ring. The CV of TF2B was qualitatively similar to that of TF2A (Fig. 2C).

In the anodic scan of TF3 (Fig. 2D), the peak at the potential (E_a = +0.38 V) is assigned to oxidation of the pyrogallol group on the gallate to the semiquinone radical and the oxidation of the catechol group on the benzotropolone ring to quinone (Peak I/II). Compared with the CV profiles of TF2A and TF2B, the shoulder due to the oxidation of the catechol group on benzotropolone is not observed. This is because TF3 has a double gallate, whereas TF2A and TF2B have a single gallate. The peak is dominated by oxidation of the pyrogallol group on the gallate than that of the catechol group on benzotropolone. This is supported by the fact that the ratio of the cathodic-to-anodic current (I_c/I_a = 0.58) is smaller than that of TF2A and TF2B. The assignments of Peaks IV and I′ are the same as that for TF2A and TF2B.

In an anodic scan of EGCG (Fig. 2E), a doublet oxidative peak is observed. The peak at a lower potential (E_a = +0.22 V) is assigned to the oxidation of the pyrogallol group on the flavonoid skeleton to the semiquinone radical (defined as Peak III),

and the peak at a higher potential (E_a = +0.33 V) is assigned to the pyrogallol group on the gallate to the semiquinone radical (Peak II).[12,25] The barely discernible peak at a higher potential (E_a = +0.74 V) is assigned to further oxidation of the semiquinone radical to the quinone form on the gallate group (Peak IV) and the B-ring pyrogallol group (Peak V).

Here, we demonstrate the advantage of the CNT electrode. Figure S1 (Supporting Information) shows the CVs of TF1 and EGCG at a conventional carbon paste electrode. The distinct peak and the current due to TF1 and EGCG, like at the CNT electrode, were not observed. It is difficult to detect theaflavins with a carbon paste electrode. In fact, the previous report was conducted at a higher concentration. This demonstrate the CNT's functionalities, such as the high sensitivity, high reproducibility.

The effect of the potential scan rate on the CV response for the oxidation of theaflavins and EGCG was investigated in the range of 10 – 500 mV s^{-1} (Fig. S2, Supporting Information). The anodic peak current is proportional to the square root of the scan rate, which indicates that the oxidative current is controlled by the diffusion of polyphenols from the bulk solution to the electrode surface in the range of 10 – 100 mV s^{-1}. From the obtained results, a scan rate of 50 mV s^{-1} was selected for further experiments, because the current is proportional to the theaflavins and EGCG concentrations. Chronocoulometric measurements were also conducted to evaluate the diffusion coefficient of the polyphenols from the bulk to the surface, as shown in Fig. S3 (Supporting Information). The diffusion coefficient (D) is based on the Cottrell equation,

$$Q = 2nFACD^{1/2}t^{1/2}\pi^{-1/2} + nFA\Gamma_0 + Q_{dl}, \quad (1)$$

where F is the Faraday constant, n is the number of electrons transferred to the electrode, C is the concentration of the analyte, A is the area of the electrode, t is the time after the potential step, Q_{dl} is the double-layer charge, and Γ_0 is the surface coverage of the analyte determined from a plot of square root of time *versus* charge. We used n = 2 for theaflavins because the corresponding potential is mainly controlled by reaction of the catechol group. We used n = 2 for EGCG because the corresponding potential originated from the pyrogallol group of both the B-ring and the gallate moiety. D is determined from a plot of square root of time *vs.* charge and those for theaflavins and EGCG at the CNT electrode were 8 – 15 × 10^{-6} cm^2 s^{-1}.

Electrochemical quantification for each theaflavin

The peak current (background subtracted) *vs.* concentration at Peaks I/II of four theaflavins and EGCG are shown in Fig. 3. Reproducibility is an essential requirement for quantitative detection. The CV is advantageous for this purpose because a repeat scan can enhance the reproducibility by the stability of the electron transfer rate and the cleaning effect of the electrode surface. The linear functions for determining the four catechins using the peak current (I_p) *vs.* concentration ([TF]) plot were I_p (μA) = 0.35 + 0.076[TF1] (μM) r = 0.999, I_p (μA) = 0.37 + 0.076[TF2A] (μM) r = 0.999, I_p (μA) = 0.36 + 0.066[TF2B]

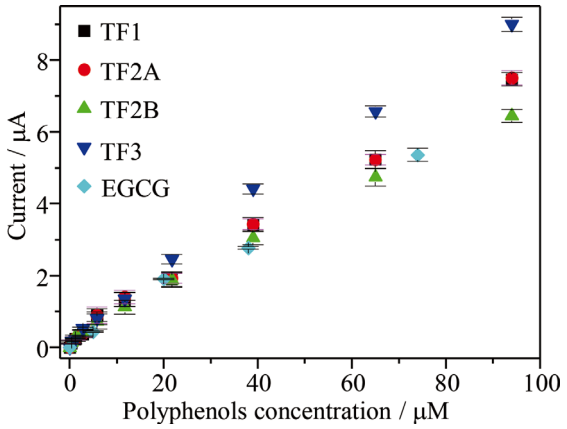

Fig. 3 CV peak current (background subtracted) at +0.35 V *vs.* concentration plot using the data in Fig. 2.

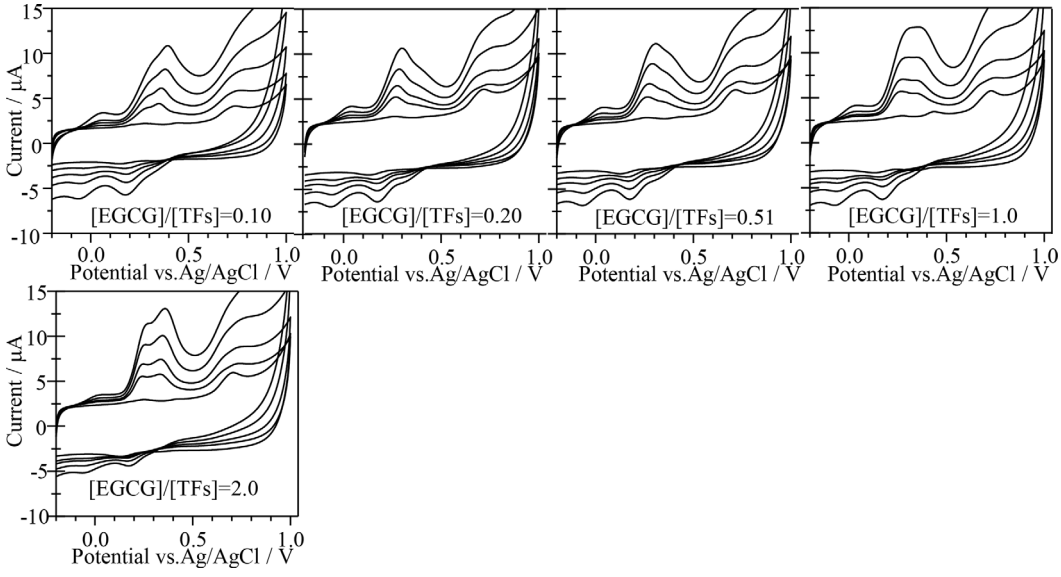

Fig. 4 Simulated CVs of mixture solution of theaflavins (TFs) and EGCG. Mass ratio of [EGCG]/[TFs] are shown in the figures. TFs is a 1:2 mixture of TF1 and TF2A. The concentrations are 0, 22, 39, 65, and 94 μM. The electrolyte used was in 50 mM pH 5.3 citric acid buffer solution. The scan rate was 0.05 V s^{-1}.

(μM) r = 0.999, I_p (μA) = 0.36 + 0.0732[TF3] (μM) r = 0.998, I_p (μA) = 0.15 + 0.079[EGCG] (μM) r = 0.996, with a linear range of 5 – 94 μM for all polyphenols. The detection limits (signal-to-noise ratio >3) for all polyphenols were estimated to be in the range of 0.11 μM. This result shows that the individual theaflavins can be quantified if the solution contains a single kind of theaflavins. This is the first report of concerning theaflavin quantification at a range of 5 – 94 μM concentration with CV.

Quantification of polyphenols in mixture solutions

The CV profile of black tea is considered to be composed of the sum of the individual theaflavins and catechins. Four theaflavins exist at various ratios in a black tea.[5-8] It is difficult the trace of individual theaflavins because the CV profiles of those theaflavins are similar. The sensitivities, defined as the slopes of the current *vs.* mass concentration (mg/dL) plot of four theaflavins, are similar. Therefore, the peak current at around +0.35 V (Peak I/II) can quantify the total theaflavins (TFs) concentration or one theaflavin (e.q., TF2A) equivalent. The sensitivities of EGCG are also similar to those of four theaflavins. Actual tea catechins are catechin, epicatechin, epigallocatechin, epicatechingallate, and EGCG. EGCG is the most abundant catechin; then, several researchers have reported that the electrochemical determination of total catechins in green tea is performed for the EGCG equivalent.[12,15,19-21] The quantification of total catechins in this experiment is determined as the EGCG equivalent. In this research, we address theaflavins as major polyphenols and catechins as minor ones. A simulated CV for a black tea was conducted. A mixture solution was prepared to achieve the composition ratio of [EGCG]/[TFs]. Figure 4 shows the simulated CV. We intentionally prepared the mixture solution of theaflavins and EGCG. First, 5 mL of a 0.2 mM TF1 solution and 10 mL of a 0.2 mM TF2A solution were mixed. This is defined as a TFs solution. On the other hand, the TFs solution and the 0.2 mM EGCG solution were prepared. Finally, the TFs and EGCG solutions were mixed for the desired the mass ratio [EGCG]/[TFs]. In Fig. 4, we present the mixture solution of the mass ratio [EGCG]/[TFs] = 0.10, 0.20, 0.51, 1.0, and 2.0. When the ratio of EGCG to TFs ([EGCG]/[TFs]) increases, Peak I/II (II) becomes broader. When the ratio of [EGCG]/[TFs] surpasses 2, two peaks are observed. The lower peak is due to the pyrogallol group of flavonol in EGCG.

Figure 5 shows the current (ΔI, background subtracted) *vs.* concentration of the total polyphenol ([TFs+EGCG]) at Peak I/II (Peaks I and II overlap each other), where the mass ratios [EGCG]/[TFs] = 0.10, 0.20, 0.51, 1.0, and 2.0 were used. This indicates that the current change at Peak I/II is in good agreement with the concentration of the sum of TFs and EGCG. The linear function of catechins, determined by Peak I/II in the current *vs.* concentration plot, was I_p (μA) = 0.20 + 1.23[TFs+EGCG] (mg/dL) r = 0.985. This line is near to that for the solution containing 100% theaflavins or EGCG. This shows that the peak current around at +0.35 V (Peak I/II) can quantify the total polyphenol concentration. Although we adopt a current for quantification, a charge can also be used for quantification. There is no difference between the current and the charge.[29] The voltammograms between theaflavins and EGCG are very different. When the ratio of [EGCG]/[TFs] is changed, the voltammogram is changed; in a word, the CV shape is related to the ratio of [EGCG]/[TFs]. Therefore, the CV profiles roughly estimate the ratio of [EGCG]/[TFs].

Quantification of polyphenols in a real black tea sample

Figures 6A and 6B show the CVs of real black tea samples at various dilutions. The total polyphenol concentration of samples 1 and 2 by HPLC are 32.0 and 31.9 mg/dL, respectively. The concentrations of individual TFs and catechins are given in Table S1 (Supporting Information). [TFs] denotes the sum of four TFs. [EGCGeq] denotes the sum of eight catechins, such

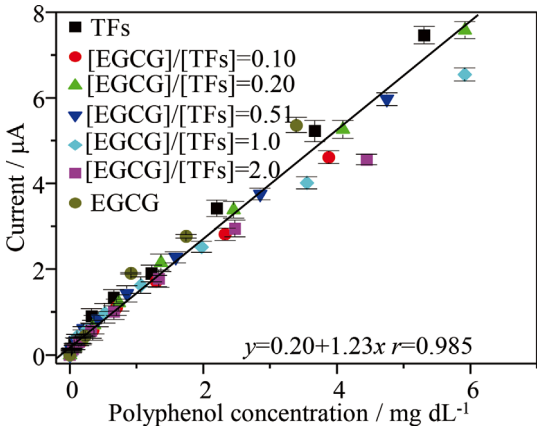

Fig. 5 CV current (background subtracted) *vs.* concentration plot for polyphenol mixture solutions with various contents of individual theaflavins and EGCG. The black line represents the least-squares fitting line. Parts of the CVs are shown in Fig. 4.

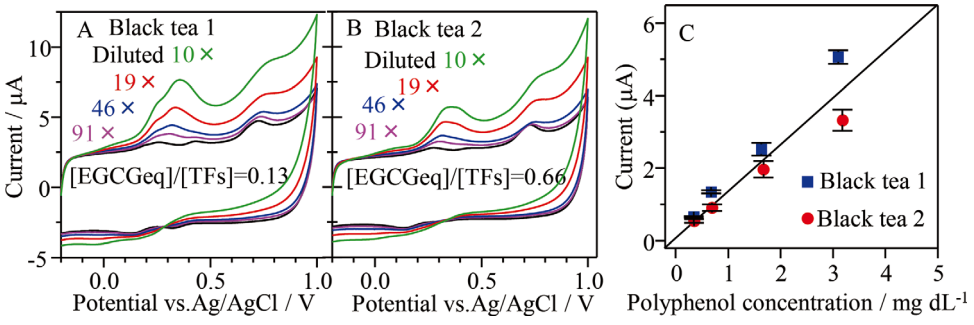

Fig. 6 (A, B) CVs of real black tea samples 1 and 2 for various dilutions. The black line is background. The ratio of [EGCGeq]/[TFs] determined by HPLC. (C) The background-subtracted current *vs.* diluted concentration based on HPLC data is plotted. The fitting line based on their simulated CV in Fig. 5. The conditions for CV were the same as in Fig. 2.

as catechin, gallocatechin, catechingallate, gallocatechingallate, epicatechin, epigallocatechin, epicatechingallate, and EGCG. We adopted the CV current of a real sample due to oxidation of the total amount of eight catechins as the EGCG equivalent, which denotes [EGCGeq]. This procedure is used for an electrochemical determination of the total catechin concentration in green tea by many researchers.[10-12,15,19-21] The ratio of [EGCGeq]/[TFs] of samples 1 and 2 by HPLC are 0.13 and 0.66, respectively. Figure 6C shows a plot of the total polyphenols (TFs+EGCGeq) concentration in a real sample *vs.* the CV current (background subtracted) of various diluted samples. When the relationship of the current *vs.* diluted concentration based on HPLC data is plotted, they have a strong correlation with the fitting line based on their simulated CV (Fig. 5). Although being slightly different, there is a good agreement between the values obtained by CV and HPLC. The CV value of black tea 1 is overestimated when compared with the HPLC value, whereas that of black tea 2 is underestimated. This is probably because (i) black tea 1 contained more other polyphenols (*e.g.*, thearubigin) than black tea 2, and (ii) when the value of [EGCG]/[TFs] increases, the CV current is apt to saturate at a higher concentration region (see Fig. 5). The CV shapes of real samples are similar with their simulated CVs with a mixture of theaflavins and EGCG, which suggests that this technique can provide information regarding the levels of theaflavins and catechins.

Conclusions

We demonstrated the electrochemical quantification of polyphenols composed of theaflavins and catechins in a black tea infusion for the first time. The peak current at around +0.35 V in a CV measurement can quantify the total amount of polyphenols in a black tea. The shape of the CV curve can roughly estimate the ratio of catechins to theaflavins. The shapes of the CVs for real samples and their simulated CVs with a mixture of theaflavins and catechins are similar, which suggests that this technique can provide information regarding the levels of theaflavins and catechins. The values of total polyphenols for real samples from CV measurements are in good agreement with those from HPLC. This procedure has the possibility of extension to polyphenol analysis to foods and beverages.

Acknowledgements

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Supporting Information

CVs of TF1 and EGCG at a carbon paste electrode, CVs of individual theaflavins and EGCG at various sweep rates, also an plot of the peak position, a chronocoulometric plot of the theaflavins and EGCG, the concentrations of individual TFs and catechins in real samples. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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