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*Short Communication*

# Authentical Screening of Tea Beverages Based on Voltammetric Profile

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The voltammetric profiles of tea beverages vary among brands and products due to the presence of different types and concentrations of electro-active compounds. These differences are determined by the factory process, recipe and tea leaf selection. In this communication, we proposed a quick and low-cost method for recording the electro-active compound profile in tea beverages based on the direct insertion of a three-electrode system into beverage liquid. The polyphenol compounds in tea beverages can be oxidized during a differential pulse voltammetric scan. By using the peak criterion with a ratio calculated from major peaks, DPV profiles can be used to identify twelve different tea beverages in this work. The stable profile recording performance along with clustering analysis suggests that the proposed method can be effectively used for authentic identification of tea beverages. We believe that the proposed methodology can be further extended to other food quality screening applications.

**Keywords:** Electrochemistry; Tea beverage; Glassy carbon electrode; Cluster analysis; Voltammetric profile

## 1. INTRODUCTION

Tea beverages are widely praised by consumers because of their natural, healthy and rich nutrition. Since the 1990s, global tea beverages have increased at an annual rate of 17%, becoming the third generation of drinks after carbonated drinks and pure water. Therefore, the quality and authentic identification of tea beverages have attracted increasing attention. To date, high-performance liquid chromatography [1], capillary electrophoresis [2], gas chromatography-mass spectrometry [3], ultraviolet absorption [4], infrared spectrophotometry [5] and near-infrared spectroscopy [6] have been successfully used in the identification of tea and tea beverages. Although these methods could be used for the determination of the quality and authenticity of tea beverages, the complicated sample preparation process and expensive instruments restricted their field applications. In contrast, electrochemical analysis is an alternative approach that can be used for food quality evaluation.

The taste of different tea beverages mainly depends on the content and combination of flavour chemicals. As tea is rich in active substances, the composition of active substances in different brands of tea beverages will be different due to differences in the selection of raw tea leaves and the production process. Our previous works demonstrated that this method can be used for plant species determination based on the extract of plant tissues [7,8]. The electrochemically active substances in the analyte contribute current values at different potentials due to the redox reaction. This electrochemical fingerprint depends on the types and concentrations of electro-active compounds. Therefore, this method has a strong potential value for the identification of tea beverages.

In this communication, we first attempt to use a glassy carbon electrode (GCE) to record the voltammetric profiles of tea beverages. Four brands of black tea, green tea and oolong tea beverages were selected for investigation. The differences among the voltammetric profiles can be used for tea beverage identification, which has great potential for field food authenticity screening.

## 2. EXPERIMENTAL

**Table 1.** Information on twelve tea beverage samples.

| Brand | Type | Ingredients | Origin |
|---|---|---|---|
| Brand 1 | Black tea | Water, sugar, fructose syrup, black tea, concentrated lemon juice, honey, sodium citrate, vitamin C | Nanjing Jiangsu |
| Brand 2 | Black tea | Water, sugar, fructose syrup, black tea powder, food additives | Kunshan Jiangsu |
| Brand 3 | Black tea | Water, black tea,edible essence, food additives | Hangzhou Zhejiang |
| Brand 4 | Black tea | Water, sugar, salt, instant black tea, food additives, edible essence | Hangzhou Zhejiang |
| Brand 5 | Oolong | Water, oolong tea, concentrated oolong tea, vitamin C, food additives | Changsha Hunan |
| Brand 6 | Oolong | Water, oolong tea, food additives | Suzhou Jiangsu |
| Brand 7 | Oolong | Water, oolong tea, food additives | Hangzhou Zhejiang |

| | | | |
|---|---|---|---|
| Brand 8 | Oolong | Water, sugar, oolong tea, ice sugar, concentrated oolong tea, honey, food additives | Zhengzhou Henan |
| Brand 9 | Green tea | Water, green tea, food additives | Hangzhou Zhejiang |
| Brand 10 | Green tea | Water, sugar, jasmine tea, green tea, honey, concentrated green tea, food additives | Suzhou Jiangsu |
| Brand 11 | Green tea | Water, sugar, green tea, jasmine tea, oolong tea, food additives | Xi’an Shanxi |
| Brand 12 | Green tea | Water, high fructose corn syrup, sugar, longjing tea, jasmine tea, black tea, food additives, edible essence, salt | Hangzhou Zhejiang |

All twelve tea beverages were purchased from a local supermarket without any treatment. Table 1 shows the information about all twelve samples.

All electrochemical determination processes were carried out using a portable CHI210c electrochemical workstation. A commercial glassy carbon electrode (GCE), an Ag/AgCl electrode and a Pt electrode were used as the working electrode, reference electrode and counter electrode, respectively.

Differential pulse voltammetry (DPV) scans were used to record voltammetric profiles. The glassy carbon electrode was first polished using alumina slurry after a water wash. Then, the three-electrode system was inserted into 5 mL of tea beverage. The electrochemical voltammogram recording was conducted at 0–1.3 V, with a pulse amplitude of 50 mV, a pulse width of 0.05 s and a pulse period of 0.5 s.

Voltammetric data standardization was carried out to establish quantitative criteria of recognition [9], where the ratios between the current and the maximum peak current were obtained at different potentials. PCA and cluster analysis were performed using R.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the direct DPV responses of all twelve tea beverages recorded on the GCE surface. Each sample was investigated using 5 individual GCEs. As shown in the figure, the five voltammetric scans showed profiles, indicating that the proposed direct voltammogram recording procedure is capable of recording a stable profile. This stable response can be ascribed to the mineral compounds in the tea beverages, which served as electrolytes for free biomolecules participating in the electrochemical reaction [10–13].

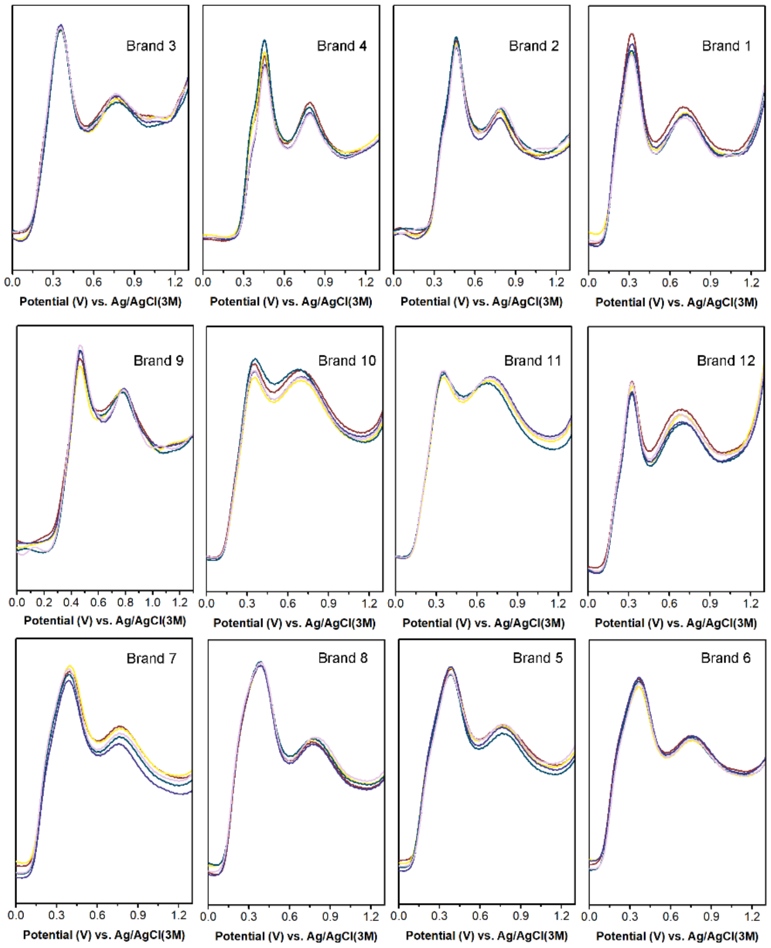

**Figure 1.** DPV curves of twelve tea beverages recorded on a GCE.

All voltammetric scans of tea beverages showed two major oxidation peaks at approximately +0.4 V and +0.8 V. According to many previous reports, these two peaks can mainly be ascribed to the oxidation of catechin [14]. Catechin is a phenolic active substance extracted from natural plants such as tea leaves, which can be oxidized at a low overpotential. The electro-oxidation of catechin involves two steps, in which the 3,4-dihydroxyl groups were first oxidized to an *o*-quinone form at a low potential. Then, oxidation of hydroxyl groups of the resorcinol moiety can occur at a relatively high potential. Except for catechin, many other polyphenolic compounds can be oxidized at these potential ranges. Therefore, broad peak responses can be observed in some samples, such as Oriental leaves-Oolong tea, Master kong-Oolong tea and Chunchashe-Oolong tea. Although it is hard to separate the peaks into individual components because these compounds have very similar structures, the overall voltammetric pattern can be used for authentic identification of tea beverages.

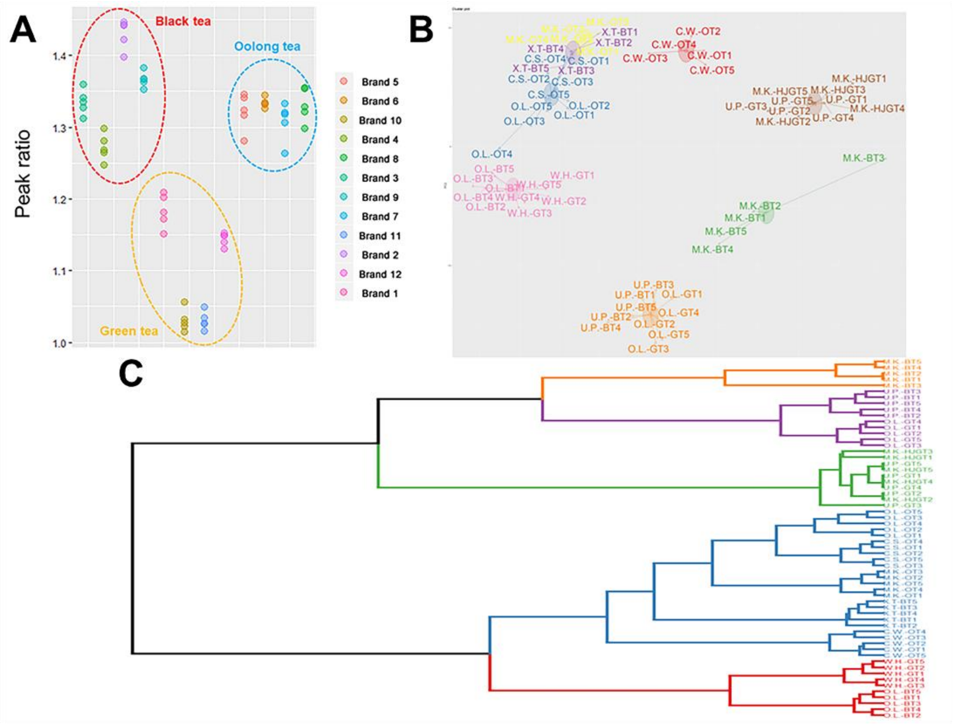

**Figure 2.** (A) Plots of $i_{(+0.4\ V)}$ *vs.* $i_{(+0.8\ V)}$ for tea beverage samples in this study using the normalized current values measured in DPV. (B) PCA diagrams of twelve tea beverages obtained from normalized currents recorded by voltammetric scans. (C) Clustering analysis twelve tea beverages obtained from normalized currents recorded by voltammetric scans.

Then, the voltammetric data were normalized before chemometric analysis. The ratio of the peak currents at approximately 0.4 V and 0.8 V was calculated (Figure 2A). As shown in the figure, the black tea and oolong tea samples showed ratios between 1.23 and 1.46, while all green tea samples showed ratios below 1.23. We believe this phenomenon can be ascribed to the selection of different raw tea leaves. Black tea and oolong tea are fermented tea, and the chemical reaction of polyphenols changes the chemical composition of fresh leaves and produces theaflavins, theophyllin and other components. The content of polyphenols with small molecular weights in black tea and oolong tea should be higher than that of green tea. Therefore, more electro-active compounds can be oxidized at a lower potential range and consequently increase the ratio value [15–20]. Due to the similar ratio values of black tea and oolong tea, the peak ratio is insufficient for direct authentic identification of tea beverages.

A statistical method can more accurately identify the authenticity of tea beverages. Therefore, we submitted the voltammetric data for principal component analysis (PCA). Figure 2B shows the PCA results of all 60 voltammetric scans. It can be seen that there are several groupings of tea beverages. The PCA extracted two components that explain approximately 74% of the variation in the data. The first and second components explain 52% and 22% of the directly recorded voltammetric profiles, respectively. The PCA successfully separated the Master kong-black tea, Chaliwang-oolong tea, Master kong-oolong tea and Xiaomingtongxue-black tea. In addition, Uni-president-black tea and Oriental leaves-green tea were grouped together. Master kong-honey-jasmine green tea and Uni-president-green tea were grouped together. Oriental leaves-black tea and Wahaha-black tea were grouped together. In addition, Oriental leaves-oolong tea and Chunchashe-oolong tea were grouped together. However, even though these samples were grouped with each other, clear boundaries were observed between different brands. Except for the Master kong-honey-jasmine green tea and Uni-president-green tea, all the rest of the data were well separated. Therefore, our work suggests that the voltammetric data of tea beverages can be used as a database and subsequently used for unknown sample identification. Due to the high reproducibility of the voltammetric profiles, clustering analysis can be more effectively used for tea beverage identification in field food safety screening.

## 4. CONCLUSION

In this communication, we proposed direct insertion of a three-electrode system into tea beverages to measure voltammetric profiles. The recorded voltammetric profiles varied among the tea beverages, and these differences were used for authentic identification. Due to the high reproducibility of the profiles, clustering analysis can be more effectively used for tea beverage identification.

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