



## Screening and authentication of tea varieties based on microextraction-assisted voltammetry of microparticles



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### ABSTRACT

A simple electrochemical methodology for screening and authentication of green, black and red tea varieties is proposed. It is based on the record of the voltammetric response of microparticulate films of antioxidant compounds resulting from an ethanolic micro-extraction of commercial tea herbal preparations in contact with aqueous buffers. The obtained voltammetric responses led us to differentiate between diverse tea varieties upon application of bivariant and multivariate chemometric techniques, including discrimination of mixtures of teas with sensitivity estimated of  $5.0 \mu\text{A mg}^{-1}$  with a detection limit of 0.01 mg of tea sample. Under the proposed conditions 100% discrimination rate was achieved for binary mixtures of teas between 10:1 and 1:10 w/w composition.

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### 1. Introduction

Tea, one of the most widely consumed beverages around the world, is manufactured in three basic forms, green, black and oolong tea. Fresh tea leaves from *Camelia sinensis* are unusually rich in the flavanol group of polyphenols known as catechins which may constitute up to 30% of dry leaf weight. Other polyphenols include flavanols and their glycosides, and depsides such as chlorogenic acid, coumarylquinic acid, and one unique to tea, theogallin (3-galloylquinic acid) [1]. The composition of green tea, consumed primarily in China, Japan, and a few countries in North Africa and the Middle East, is similar to that of fresh tea leaves except for a few enzymatically catalyzed changes which occur extremely rapidly following plucking. Black tea is prepared under oxidizing conditions where an active polyphenol oxidase catalyzes the aerobic oxidation of the catechins when the leaf cell structure is disrupted. Such processes yield quinones which can undergo condensation reactions and result in a series of compounds, including bisflavanols, theaflavins, epitheaflavic acids, and thearubigens, most of which can form complexes with caffeine, a minority compound in tea leaves [1,2]. Oolong tea is intermediate in composition between green and black teas and can be considered as a partially oxidized tea.

Authentication and characterization of the different tea varieties has received considerable attention [3]. The differentiation between green and black tea can be achieved by using tracer compounds such as theanine [4] or analyzing the flavanol pattern, typically expressed in terms of the ratio between different polyphenolic compounds (catechins vs. total phenolics and/or catechins vs. theaflavins and/or total phenolics/total catechins). Among other techniques, thin-layer chromatography [5], conventional and NIR infrared spectroscopies [6,7], capillary zone electrophoresis [8] and microscopy [9], have been reported for authentication purposes [10]. Discrimination of tea varieties, apart from the obvious implications in food analysis, is of interest with regard to their antimicrobial [11] and therapeutic applications [12]. For this purpose, several chromatographic and spectroscopic techniques have been proposed [6,7,13–16].

In this context, solution-phase electrochemistry has been applied for tea variety discrimination [17,18], evaluation of its fermentation degree [19,20] and catechin [21] or total polyphenolic content [22] determination. These methods, as well as chromatographic and spectrophotometric ones, need a relatively laborious sample treatment addressed to pass the tea leaf components to a suitable solution. As a result, there is opportunity for producing the aerobic oxidation of most of the relevant polyphenolic compounds to be analyzed, thus decreasing the representativity of the sample.

Here, we report a simple electrochemical methodology for screening and authentication of tea varieties based on the record of the electrochemical response of the polyphenolic components of tea leaves. Both catechins and theaflavins possess electroactive

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polyphenol motifs, displaying electrochemistry similar to that of flavonoids, based on proton-assisted oxidation of catechol units to quinones [23–29]. The reported method consists of an in situ microextraction-assisted voltammetry of microparticles (VMP) assay. This is based on the record of the voltammetric response of a microparticulate film of the components on an ethanolic extract of the tea leaves in contact with aqueous buffers. The relevant point to emphasize is that the proposed methodology can discriminate between tea varieties from the chemometric analysis of the complete voltammetric pattern without the need for identifying and quantifying the individual compounds present in the sample.

The microextraction process permits, after evaporation, the formation of microparticulate films of the extracted compounds on the electrode surface which are representative of composition of tea leaves [30–32]. Polyphenolic compounds in general produce a well-defined electrochemistry, as reported for catechin [33–35]. This scheme follows the essential guidelines of the VMP methodology, a solid-state electrochemical technique developed by Scholz et al. which provides analytical information on sparingly soluble solids [36,37]. This technique has previously been used to study the solid state electrochemistry of flavonoid compounds [38–45]. In order to study the possibility of out-lab measurements, VMP experiments were conducted in non-degasified aqueous acetate and phosphate buffers using laboratory and portable equipments. The use of non-degasified solutions provides the opportunity for electrochemically generation of reactive oxygen species (ROS) by electrochemical reduction of dissolved oxygen [46–48], the reactivity of such species with tea compounds being usable for screening purposes. The radical scavenging activity of plant extracts has also been studied electrochemically using chemical generation of ROS [49,50]. The antioxidant capacity of tea leaves [51] and other vegetables [52] has been studied, using VMP, by Komorsky-Lovric et al. The microparticulate nature of the prepared films has been assessed using electrochemical scanning microscopy (SECM). This is an electrochemical technique developed by Bard and Mirkin [53] that provides information on electrochemical surface topography at the micrometer- sub-micrometer domain which can be applied for characterizing microparticulate films of flavonoid and pigments [54].

## 2. Experimental

Catechin and chlorogenic acid were purchased from Sigma–Aldrich (Madrid, Spain) and Quercetin-3-rutinoside from Merck (Darmstadt, Germany). Aqueous acetic acid/sodium acetate buffer solutions in concentration 0.25 M and pH 4.75 and 0.10 M potassium phosphate buffer at pH 7.0 were used as supporting electrolytes for electrochemical measurements using nanopure water and reagents from Panreac (Barcelona, Spain). Tea samples were provided by TeaShop, East-West Co. (Valencia, Spain) comprising green teas (Djaerling blend, Bandra, Kukicha, Japan sencha, Chock and Berry), oolong teas (Pu Erh Brownie, Pu Erh Canela, Pu Erh Chai, Pu Erh Original, Pu Erh Imperial) and black teas (Ceylan uva, Assau Delakat, Strong English Breakfast, Grundpower superior, Earl gray special). All were commercial formulations for which voltammetric measurements were processed without any sample pretreatment.

Electrochemical experiments were performed at  $298 \pm 1$  K in a CH cell using either a laboratory CH 1660 potentiostat (Cambria Scientific, Llwynhendy, Llanelli UK) or Ivium CompactStat portable equipment (Ivium Technol. B.V., Eindhoven, The Netherlands). A BAS MF2012 glassy carbon working electrode (GCE) (geometrical area  $0.071 \text{ cm}^2$ ), a platinum wire auxiliary electrode and an Ag/AgCl (3 M NaCl) reference electrode were used in a typical three-electrode arrangement. Voltammetric measurements were

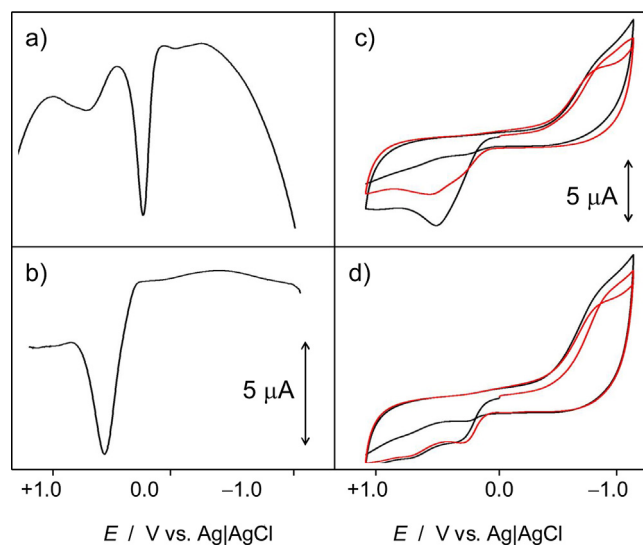
performed with a freshly prepared sample-modified GCE. For electrode conditioning, ca. 500 mg of tea leaves from different commercial formulations were powdered with an agate mortar and pestle adding 0.5 mL of ethanol (Panreac) during 2 min. 50  $\mu\text{L}$  of the resulting suspension were dropped onto the GCE surface. After solvent evaporation in air, the electrode was inserted into the electrochemical cell and electrochemical runs were performed. Cyclic voltammetry (CV) and square wave voltammetry (SWV) were used as detection modes. Principal components analysis (PCA) was applied to voltammetric data using the correlation matrix and linear regression by employing SPSS 1.2 software.

SECM experiments were performed with CH 920c equipment using a microdisk platinum electrode tip (CH 49, diameter  $20 \mu\text{m}$ ) and a Pt substrate electrode (geometrical area  $0.018 \text{ cm}^2$ ). The bipotentiostat mode was used to apply potentials to the tip ( $E_T$ ) and the electrode substrate ( $E_S$ ). The rate of scanning of the tip over the substrate was  $20 \mu\text{m/s}$  for all experiments, the distance between tip and substrate being of the order of the tip electrode radius. All measurements were performed at room temperature ( $298 \pm 1$  K) in solutions previously deaerated by bubbling argon during 15 min. A 2.0 mM solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.25 M acetic acid/sodium acetate aqueous buffer at pH 4.75 was used as a redox probe in such experiments.

## 3. Results and discussion

### 3.1. Electrochemistry of tea compounds

The SWV response of catechin and chlorogenic acid immersed into a 0.10 M aqueous phosphate buffer at pH 7.0 is shown in Fig. 1a and b. In both cases, the voltammogram is dominated by a main oxidation process at +0.20 (catechin) and +0.40 V (chlorogenic acid) vs. Ag/AgCl. Following abundant literature on catechin electrochemistry in solution phase [17–22,33–35], the oxidation mechanism proceeds in sequential steps, the first step being, as schematically depicted in Fig. 2, the proton-assisted oxidation of the 3,4-dihydroxyl groups of ring A to the corresponding *o*-quinone



**Fig. 1.** SWV of (a) catechin and (b) chlorogenic acid films of GCE immersed into 0.10 M aqueous potassium phosphate buffer, pH 7.0. Potential scan initiated at  $-1.05$  V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. CVs of (c) Bandra (green tea) and (d) Ceylan uva (black tea) films on GCE in contact with the same electrolyte. Potential scan initiated at 0.0 V in the positive (black lines) and negative (red lines) directions. Potential scan rate 100 mV/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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