

Voltammetric Determination of Tannic Acid in Medicinal Plants Using MWCNTs-Modified Electrode [†]

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Abstract: Tannins are a class of natural phenolic antioxidants represented by oligomers and polymers. Tannic acid (gallotannin) (TA) is one of the most typical compounds widely distributed in plants. It possesses a wide application area in food technology and as a part of traditional herbal medicine in the treatment of various diseases. TA is one of the standards used in the medicinal plants quality control for the plants rich of tannins. Therefore, development of sensitive and simple methods for TA quantification is of practical interest. Glassy carbon electrode modified with multi-walled carbon nanotubes (GCE/MWCNTs) has been developed for the determination of TA in medicinal plants. The improvement of TA voltammetric response has been achieved using modified electrode due to the high electroactive surface area and electron transfer rate vs. bare electrode. TA electrooxidation at the GCE/MWCNTs is irreversible surface-controlled process involving transfer of two electrons and two protons on the first step. In differential pulse mode using Britton-Robinson buffer pH 2.0 as supporting electrolyte, the linear dynamic range of 0.10–7.5 μM with the detection limit of 0.038 μM have been obtained. Method has been applied for the analysis of infusions and decoctions of tannin-containing medicinal plants and compared to the spectrophotometric method. A positive correlation has been observed with ferric reducing power reflecting total content of phenolic compounds in the sample.

Keywords: voltammetry; chemically modified electrodes; carbon nanotubes; phenolic antioxidants; tannic acid; medicinal plants; phytoanalysis

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1. Introduction

Tannins are a class of natural phenolic antioxidants represented by oligomers and polymers. Tannic acid or gallotannin (TA) (Figure 1) is one of the most typical compounds widely distributed in plants [1]. It possesses a wide application area in food technology [2,3] and as a part of traditional herbal medicine in the treatment of various diseases [4–6]. TA is one of the standards used in the medicinal plants quality control for the plants rich of tannins. Therefore, development of sensitive and simple methods for TA quantification is of practical interest.

The presence of phenolic moieties in the TA structure makes it electroactive and able to be measured using voltammetry. Nevertheless, a lack of electrochemical methods has been reported for TA determination compared to other natural phenolics. Traditional carbon-based [7,8] and platinum [9] electrodes show low sensitivity and selectivity of TA response that are the main limitations of their practical application. Various chemically modified electrodes are developed to date to solve this problem. Carbon nanomaterials [10–13], porous nanomaterials [14–16], metal nanoparticles [17,18], electrodeposited nickel(II) hexacyanoferrate [19], polymeric coverages [20,21], and 1-benzoyl-3-(pyrrolidine) thiourea film [22] have been shown as effective electrode surface modifiers for TA quantification. In most cases, adsorptive preconcentration for 2.5–5 min is used to

improve analytical characteristics of TA. This step increases the measurement duration and can lead to the co-adsorption of other components from the real samples. Furthermore, the analytical characteristics of the existing methods are not impressive (the linear ranges cover mainly μM concentrations with the detection limits of $n \times 10^{-7} \text{ M}$).

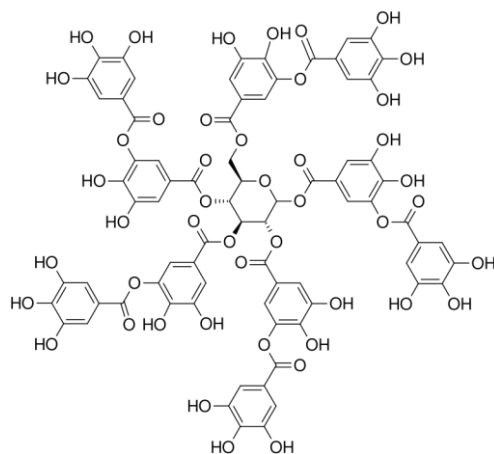


Figure 1. TA structure.

The current work is focused on the development of fast and sensitive voltammetric approach for the TA determination using glassy carbon electrode modified with multi-walled carbon nanotubes (GCE/MWCNTs) and its application in the medicinal plants analysis.

2. Materials and Methods

TA (ACS reagent grade) from Sigma-Aldrich (Saint Louis, MO, USA), 99% gallic and 99% ascorbic acids, 98% quercetin dihydrate from Sigma (Steinheim, Germany) and 97% rutin trihydrate from Alfa Aesar (Heysham, UK) were used. Their standard 10 mM (1.0 mM for rutin) solutions were prepared in ethanol (rectificate). Exact dilution was used for the preparation of less concentrated solutions.

MWCNTs (o.d. 40–60 nm, i.d. 5–10 nm, and $l = 0.5\text{--}500 \mu\text{m}$) from Sigma-Aldrich (Steinheim, Germany) were applied as electrode surface modifier. Sodium lauryl sulfate (97.2% purity) from Panreac (Barcelona, Spain) was used as dispersive agent for MWCNTs. Homogeneous suspension of MWCNTs in 1% sodium lauryl sulfate (0.5 mg mL^{-1}) was prepared by sonication for 30 min in an ultrasonic bath (WiseClean WUC-A03H) (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea).

Commercial medicinal plant materials (*Quercus* sp. cortex, *Bergenia crassifolia* (L.) Fritsch rhizomata, *Potentilla erecta* (L.) Raeusch. rhizomata, *Alnus incana* (L.) Moench and *Alnus glutinosa* (L.) Gaertn. fructus, *Sanguisorba officinalis* L. rhizomata et radices) were studied. Infusions and decoctions were prepared using a standard Pharmacopoeia procedure [23].

Other reagents were c.p. grade and used as received. Distilled water was used for the supporting electrolytes preparation. The laboratory temperature was $(25 \pm 2 \text{ }^\circ\text{C})$.

Electrochemical measurements were conducted on the potentiostats/galvanostats $\mu\text{Autolab}$ Type III (Eco Chemie B.V., Utrecht, The Netherlands) with Nova 1.7.8 software and $\mu\text{Autolab}$ PGSTAT 302N with the FRA 32M module (Metrohm Autolab B.V., Utrecht, The Netherlands) and NOVA 1.10.1.9 software. A glassy electrochemical cell of 10 mL with three-electrode system (working GCE of $\varnothing = 3 \text{ mm}$ (CH Instruments, Inc., Bee Cave, TX, USA) or a MWCNTs-modified GCE, an Ag/AgCl reference electrode, and a platinum wire as the auxiliary electrode) was used.

“Expert-001” pH meter (Econix-Expert Ltd., Moscow, Russian Federation) with a glassy electrode was applied for the pH measurements.

Ferric reducing power of the decoctions and infusions was measured by coulometric titration with electrogenerated ferricyanide ions [24] using coulometric analyzer “Exper-006” (Econix-Expert, Moscow, Russia) with four platinum electrodes (two of them as working and auxiliary electrodes in generating circuit and another two polarized needle electrodes in indicator circuit).

3. Results and Discussion

3.1. Electrooxidation of TA

Voltammetric characteristics of TA at the bare GCE and GCE/MWCNTs have been studied using cyclic voltammetry in Britton-Robinson buffer pH 2.0 (Figure 2). Electrode surface modification provides significant improvement of the voltammogram shape due to the 20.3-fold increase in the oxidation currents. Such effect can be explained by increase of the electroactive surface area of GCE/MWCNTs (75 ± 2 vs. 8.9 ± 0.3 mm² for bare GCE on the basis of electrochemical data for 1.0 mM ferrocyanide ions oxidation) as well as pre-concentration of TA at the electrode surface. The last assumption has been confirmed by cyclic voltammetry data for potential scan rate effect study.

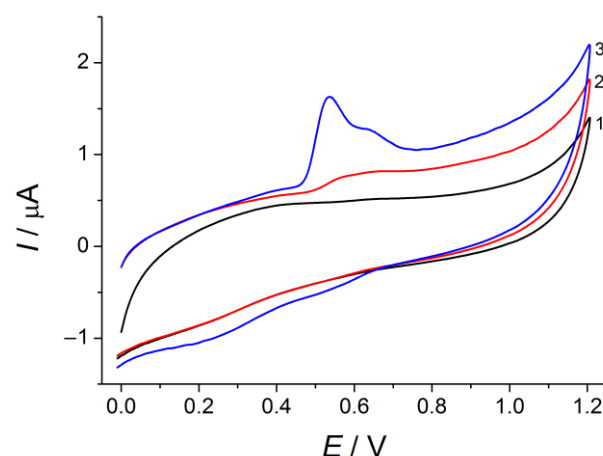


Figure 2. Cyclic voltammograms of 1.0 μM TA at the bare GCE (curve 2) and GCE/MWCNTs (curve 3) in Britton-Robinson buffer pH 2.0 (curve 1). Potential scan rate is 100 mV s⁻¹.

A 30 mV cathodic shift of the TA oxidation potential has been observed at the GCE/MWCNTs that is caused by electrocatalytic effect of MWCNTs leading to the higher electron transfer rate at the modified electrode (5.23×10^{-5} and 3.11×10^{-4} cm s⁻¹/c for bare and modified GCE, respectively, as electrochemical impedance spectroscopy data show).

TA electrooxidation is accompanied by proton transfer since oxidation potentials on both steps are shifted to less value with the pH increase from 2.0 to 7.0. The equal number of electrons and protons participate in the electrode reaction. The voltammetric response of TA is decreased with the increase of pH value and fully disappeared in basic medium due to the oxidation with air oxygen. Therefore, Britton-Robinson buffer pH 2.0 has been used in further study.

The linear plot I_p vs. potential scan rate and slope of 1.08 for $\ln I_p$ vs. $\ln \nu$ indicate surface-controlled electrode reaction. The number of electrons has been calculated using Laviron equation and equaled to two. Thus, TA electrooxidation is irreversible two electron and two proton process that agree well with reported earlier [16,17].

3.2. TA Quantification

TA determination has been performed in differential pulse mode using modulation amplitude of 75 mV and modulation time of 50 ms providing the highest oxidation

currents of the analyte. The oxidation peak at 0.49 V and a shoulder at 0.58–0.60 V are clearly pronounced on the differential pulse voltammograms of TA (Figure 3a).

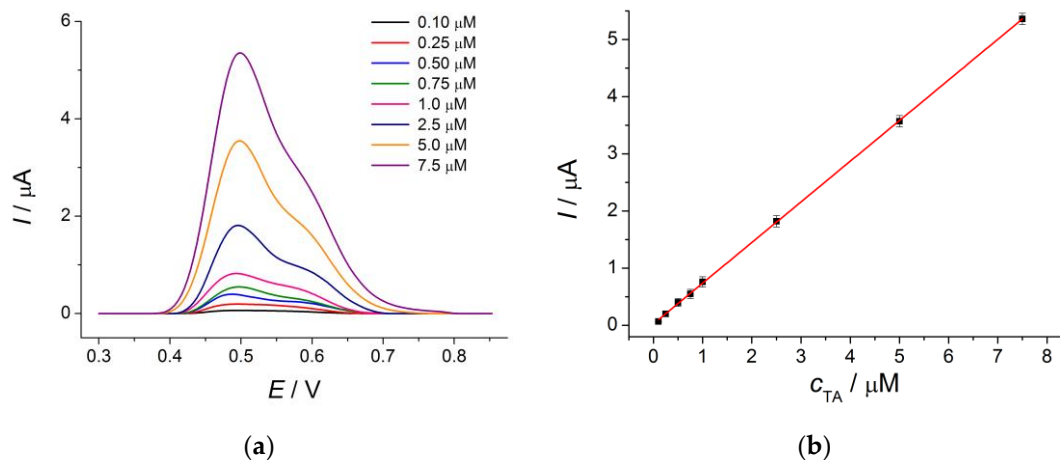


Figure 3. Differential pulse voltammetry of TA at the GCE/MWCNTs in Britton-Robinson buffer pH 2.0: (a) Baseline corrected voltammograms for 0.10–7.5 μM TA at modulation amplitude is 75 mV, modulation time is 50 ms, and potential scan rate is 20 mV s^{-1} ; (b) Calibration plot for TA.

TA oxidation currents are linearly increased with the concentration in the range of 0.10–7.5 μM (Figure 3b). The detection limit of 0.038 μM has been obtained. These analytical characteristics are improved compared to reported for the electrodes also modified with MWCNTs in [10,12,13]. Moreover, the absence of preconcentration step in current work makes procedure faster and more accurate as far as co-adsorption of coexisting components is excluded.

The method developed shows high accuracy of TA determination (recovery for model systems is 98.5–100%) and reproducibility (RSD for five measurements each on the new electrode is less than 2.0%).

3.1. Real Samples Analysis

The approach has been successfully applied in the analysis of infusions and decoctions of tannin-containing medicinal plant materials (*Quercus sp. cortex*, *Bergenia crassifolia* (L.) Fritsch rhizomata, *Potentilla erecta* (L.) Raeusch. rhizomata, *Alnus incana* (L.) Moench and *Alnus glutinosa* (L.) Gaertn. fructus, *Sanguisorba officinalis* L. rhizomata et radices). A well-defined oxidation step at 0.48–0.49 V with a shoulder at 0.58–0.60 V have been observed for all samples. The signal corresponds to TA as a standard addition method indicates. The absence of matrix effects is confirmed by recovery of 96.1–101%.

The results of TA contents in medicinal plant infusions and decoctions are presented in Figure 4. The voltammetric method validated with the UV-spectroscopy [25] and a good agreement of the results has been obtained.

A positive correlation ($r = 0.8098$) of TA contents in medicinal plant infusions and decoctions with ferric reducing power has been observed. Ferric reducing power reflects total content of phenolic compounds in the sample.

4. Conclusions

Thus, novel voltammetric approach has been developed for the direct TA quantification using GCE/MWCNTs. The procedure is simple, fast, needs low sample volume (5 μL), and excludes additional reagents consumption. The method developed can be applied for the tannin-containing medicinal plants analysis and standardization.

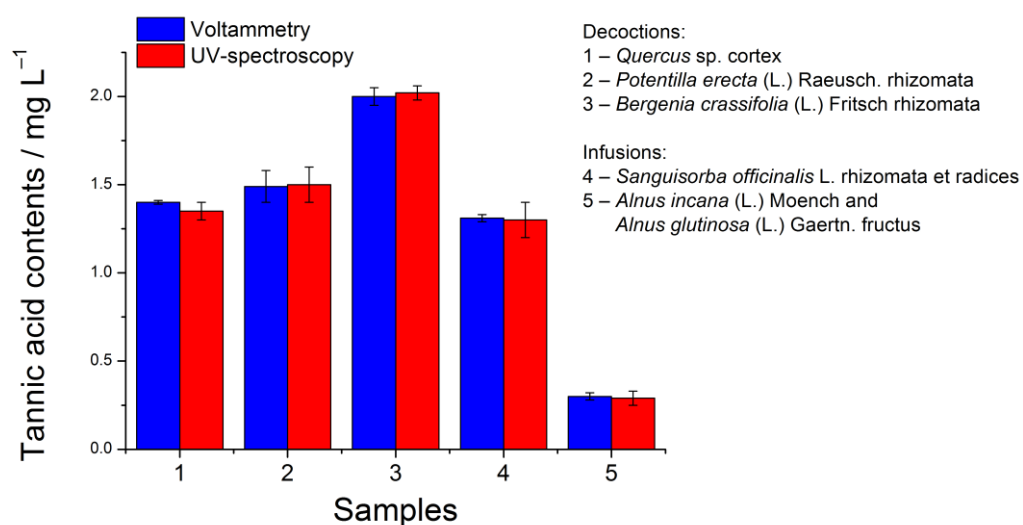


Figure 4. TA contents in medicinal plant infusions and decoctions based on the voltammetry and UV-spectroscopy data ($n=5$; $P=0.95$).

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