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Determination of Tannic Acid Using Silica Gel Modified Carbon Paste Electrode

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In this paper, silica gel modified carbon paste electrode (Si-gel/CPE) was used for the determination of tannic acid (TA) by anodic stripping differential pulse voltammetry (ASDPV). The influences of pH values, amount of silica gel, accumulation potential and time on the signal enhancement of TA were optimized, and a novel electrochemical method for the determination of TA was reported. The currents obtained from ASDPV measurements at optimum conditions were linearly correlated with the concentration of TA. Calibration curve was obtained for TA concentrations in the range of 1 - 1000×10^{-9} mol l^{-1} .The limit of detection was found to be 0.3×10^{-9} mol l^{-1}. The results from TA measurements by Si-gel/CPE were in good agreement with those obtained from the standard spectrophotometric method.

Keywords: tannic acid, silica gel, carbon paste electrode, anodic stripping differential pulse voltammetry.

1. INTRODUCTION

Tannic acid (TA) is a natural phenolic compound which can be found in fruits and many kinds of plants. The content of TA in fruits, tea and beer can strongly influence their taste, and hence, is an important parameter to evaluate and control the quality of these products [1]. TA is also used as additive in medicinal industry, including those used for treatment of burns and diarrhea [2, 3]. Besides, it may interact with metal in environmental water to form tannic acid-metal complexes/combination, which is toxic or with toxicants in aquatic ecosystems and may change their toxicity [4]. For these reasons, the determination of tannic acid has been of great importance. Several methods have been developed for this purpose including colorimetry [5], chromatography [6, 7] chemiluminescence [1, 8], spectrophotometry [9, 10] as well as electrochemical methods [11-15]. Compared with those methods above, electrochemical techniques have some advantages such as: high sensitivity, accuracy, simplicity, low expense and the possibility of miniaturization. Among all the carbon electrodes, carbon paste electrode (CPE) is an appealing and widely used electrode material in the fields of electrochemistry, electroanalysis, etc. due to its attractive advantages, such as simple preparation, low-cost implementation, renewability, low background current, and wide potential window [16]. Silica gel (Si-gel), a granular and porous form of silicon dioxide, possesses some excellent electrochemical properties such as high surface area, strong sorption ability and easy surface modification. For these reasons, it has been used for some analytical purposes as well as electrochemical techniques [17-25]. Si-gel was used for the determination of TA by anodic stripping differential pulse voltammetry (ASDPV) in our report for the first time.

2. EXPERIMENTALS

2.1. Reagents and equipments

All the reagents were purchased in Sigma-Aldrich. Deionized water was used in this study ($G \leq 0.055\ \mu S$). Dissolved oxygen was removed from all the solutions by purging with argon for 15 min (purity 99.99%, Linde Technoplyn, Czech Republic).

A stock solution of TA (10^{-2} M) was prepared freshly with deionized water and was kept in a dark bottom during the experiments. Briton Robinson (BR) buffer solution was used as supporting electrolyte.

A three electrode system consisting of CPEs (working), Ag/AgCl/3.0 M KCl (reference) and platinum wire (counter electrode) connected to PalmSens (Ivium Technologies, Netherland) was used for electrochemical measurement. The surface of modified CPE and unmodified CPE were regenerated by renewing and polishing them on wet filter paper before each measurement.

2.2. The Preparation of Si-gel/CPE

Si-gel (pore size 60 A^0, 5-25 μm particles size) and graphite powder 5.5-7.0 μm (CR-5, Maziva Týn n. L., s.r.o., Czech Republic) were weighed and the total mass was controlled at 0.5 g. The mass content of silica gel varied from 3 to 21%. After that, 130 μl of mineral oil (M5904, Sigma-Aldrich) was added in the powder and exhaustively hand mixed together in ceramic mortar by ceramic pestle. The resulting paste was packed into the teflon piston holder (3.0 mm inner diameter) [26]. The unmodified CPE was also prepared without the addition of silica gel. The electrode surface was polished on a wet filter paper prior using.

2.3. Standard spectroscopic method for the determination of TA

The standard spectroscopic method was performed using AOAC Official Method 952.03 which involves the reaction between TA and Folin-Denis reagent in the presence of saturated sodium carbonate [27].

2.4. Sample preparation

Si-gel/CPE was also used for the determination of TA in food samples (wine, orange juice, black tea) and river water sample. For this purpose, 1.5 g of black tea (Pigi, Total Global Beverages Czech Republic a.s.) was extracted in hot water for 10 min. After that, the sample was transferred to a 250 ml volumetric flask, and then was diluted by deionized water until the mark following by the filtration through a filter paper. The river water samples were collected from Labe River in Pardubice, Czech Republic, and were filtered through a filter paper to remove particulate matter because organic and inorganic ingredients of the sample may interfere with the analysis. The collected liquids were used for both electrochemical and spectroscopic method. White wine sample (Neuburk variety, Vinselekt Michlovský a.s., Czech Republic) and fruit juice sample (Multi-vitamin variety, Vitafit, Lidl Stifung & Co., KG, Germany) were used directly without any treatment.

3. RESULTS AND DISCUSSIONS

3.1. The enhancement effect of Silica-gel on the oxidation of TA

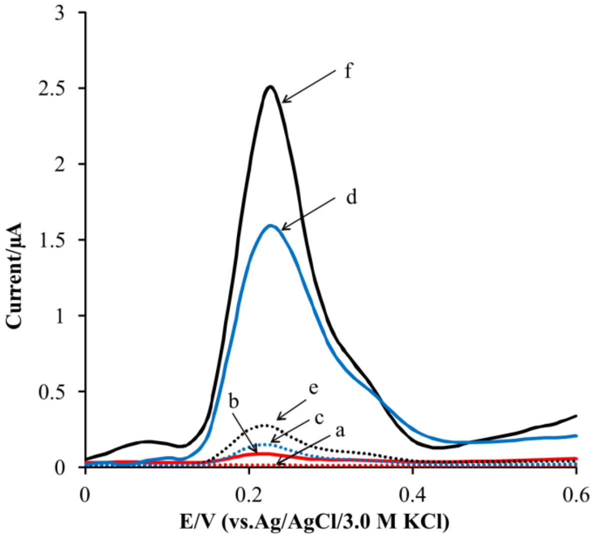

Figure 1. Differential pulse voltammetry (DPV) curves of 0.6 µM tannic acid in pH 6.0 BR buffer solution. Curves (a), (b) corresponding DPV responses in the absence of TA on CPE and Si-gel/CPE, respectively. Curve (c), (d) corresponding DPV responses without using pre-concentration step from CPE and Si-gel/CPE, respectively. Curve (e), (f) corresponding DPV responses using preconcentration step from CPE and Si-gel/CPE, respectively. Conditions: accumulation time: 240s, constant potential -0.3 V.

The responses of TA oxidation on Si-gel/CPE (15% Silica gel) and unmodified CPE were compared using differential pulse voltammetry (DPV) in a BR buffer pH 6.0. As can be seen in Fig. 1, in the presence of TA, the oxidation peak obtained from DPV (without pre-concentration step) at the potential of 0.225 V for both Si-gel/CPE (curve d) and unmodified CPE (curve c) while the oxidation current obtained from Si-gel/CPE was about 10 times higher than that obtained from unmodified CPE in the same experimental conditions. Besides, in the absence of TA, the DPV curves on Si-gel/CPE (curve b) and unmodified CPE (curve a) were very low or featureless, indicating that the peak at 0.225 V was mostly caused by the TA oxidation.

When the preconcentration step was applied, the oxidation current of TA was also observed at the same potential (0.225 V) for Si-gel/CPE (curve f) and unmodified CPE (curve e), while the current obtained from Si-gel/CPE was about 9 times higher than that obtained from unmodified CPE. The pre-concentration step significantly enhanced the oxidation of TA since the current obtained from ASDPV technique was about 1.5 times higher than that with only DPV.

The electrochemical behaviour of Si-gel/CPE was investigated by recording cyclic voltammograms in a BR buffer (pH 6.0) at various scan rates in the presence of 5×10^{-5} mol L^{-1} of TA. As indicated by Fig. 2A, the oxidation peak potential gradually shifted towards more positive direction with the increase of the scan rate. The oxidation currents increased linearly with the scan rate (Fig. 2B) ($I_a = 0.1225v + 1.6491$; $R^2 = 0.9931$). This result proved that the electrochemical process of TA at Si-gel/CPE was surface controlled.

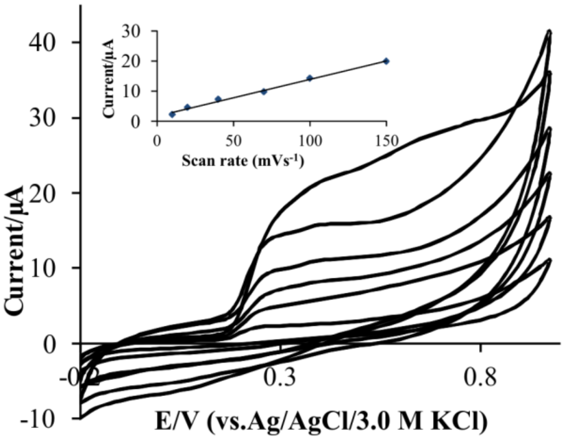

Figure 2. Cyclic voltammograms of Si-gel/CPE at various scan rates (from 10 to 150 mV s^{-1}) in the presence of 5×10^{-5} mol L^{-1} of TA. Inlet: the oxidation current of TA (5×10^{-5} mol L^{-1}) at various scan rates. Experimental condition: BR buffer pH 6.0; potential range from -200 to 1000 mV; potential step 25 mV.

The theoretical mechanism for the electrochemical oxidation of TA on the surface of Si-gel/CPE during the ASDPV can be explained as below:

(i) Preconcentration step

$SiOH_{(CPE)} + TA_{(solution)} \leftrightarrow SiOHTA_{(CPE)}$

(ii) Stripping step (positive scan from 0.0 to +0.6 V)

$SiOHTA_{(CPE)} \leftrightarrow SiOH_{(CPE)} + TA_{(ox)(solution)} + ne^-$

3.2. The determination of TA by ASDPV

Fig. 3A shows the influence of mass content of Si-gel on the oxidation peak current of TA. The peak currents of TA greatly increased with the increase of Si-gel content and reached the highest value at 15% of Si-gel. However, the oxidation peak current of TA gradually decreased with the content of Si-gel in the range from 15% to 21%. These results were in good agreement with a study on activated Si-gel modified CPE for the determination of quercetin in term of the trend [19]. However, in our study, the optimal mass content (15%) was higher than that using activated Si-gel by 6.0 M hydrochloric acid (10%). The decrease of oxidation current with the increase of the mass content of Si-gel may be caused by the reduced of conductivity resulted from a larger amount of this modifier. In this study, 15% of Si-gel was chosen as optimum for the bulk modification of CPE.

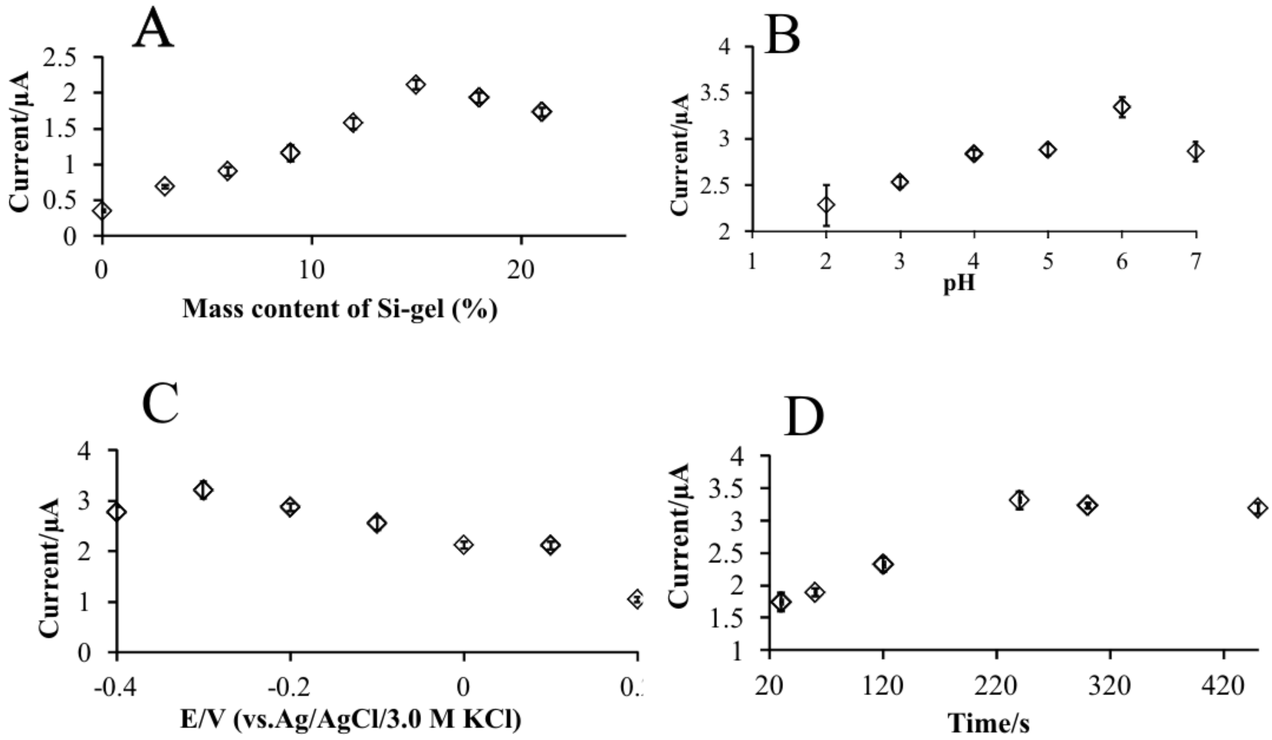

Figure 3. The oxidation peak currents of 0.6 µM TA as a function of A) mass content of Si-gel; B) pH; C) constant potential; D) accumulation time. Error bar represents the standard deviation of five measurements.

The variation of peak current with pH within the range of 2.0-7.0 is shown in Fig. 3B. It was found that the oxidation peak currents of TA on Si-gel/CPE gradually increased with the increase of pH values indicating the higher enhancement effect of Si-gel in less acidic conditions. However, badly-defined oxidation current was observed at pH 7.0 and higher pH values. In this study, BR buffer pH 6.0 was used as supporting electrolyte for the ASDPV of TA.

The variation of anodic peak current with potential is shown in Fig. 3C. The oxidation current increased rapidly with the decrease of potential in the range from 0.2 to -0.3 V. The highest current was obtained at the potential -0.3 V. After that, the current decreased from the value -0.4 V. In the literature, it was mentioned that the deposition potential for anodic stripping techniques should be about 0.3 to 0.5 V more negative than the formal potential (E_0) in the case of mercury electrode [28]. In our study, the deposition potential was 0.525 V more negative than E_0.

The influence of accumulation time in the pre-concentration step is shown in the Fig. 3D. The peak current increased rapidly with the increase of accumulation time and became relatively stable at around 240 s. After that, the oxidation current changed slightly with the increase of accumulation time, suggesting that tannic acid was accumulated quickly by Si-gel. Longer accumulation time than 240 s did not show significant enhancement effect on the oxidation of TA, revealing that the amount of TA reached the saturated amount on the surface of Si-gel/CPE.

As a result, the optimum conditions for ASDPV of TA were chosen as: supporting electrolyte (BR buffer pH 6.0), potential (-0.3 V) and accumulation time (240 s). From these conditions, calibration curve was obtained over the concentration range of TA: 1 - 1000 x 10^{-9} mol l^{-1} (Fig. 4). The limit of detection was found as low as 0.3 nM. This Si-gel/CPE electrochemical sensor is proven to be, extremely sensitive, simple renewable and easy in preparation and storage. After 45 days of storage in room temperature, the ASDPV responses of tannic acid at the concentration 10 nM of TA was insignificant different from that obtained from the fresh one, indicating the ease to preserve and good reproducibility and high stability of Si-gel/CPE.

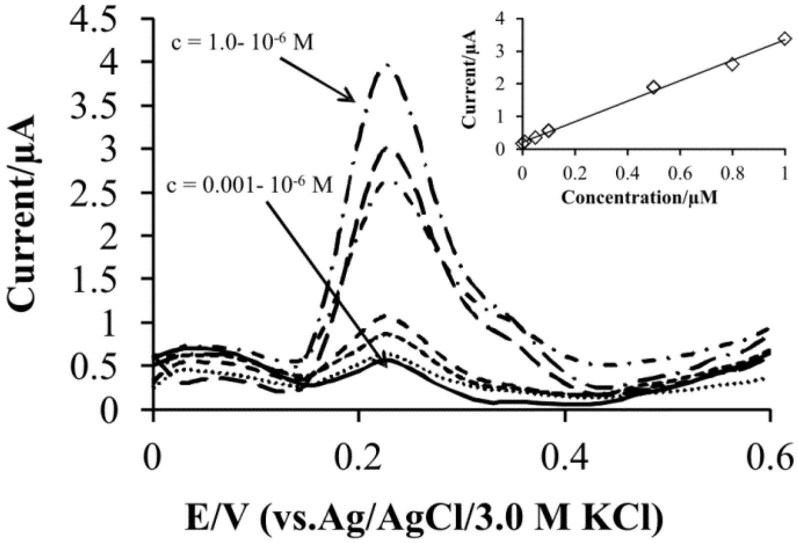

Figure 4. DPV curves of TA with various concentrations (from 0.001 to 1x10^{-6} mol l^{-1}) using Si-gel/CPE. Inlet: the plot of oxidation current vs. concentration of TA. Experimental conditions: supporting electrolyte, BR buffer solution pH 6.0; accumulation time, 240s; constant potential, -0.3 V.

The repeatability of the method was investigated by the repeated measurements of 50 nM TA and 100 nM TA (*n* = 20) and the relative standard deviation (RSD) was found to be 6.7% and 7.1 %, respectively.

The various analytical detection parameters such as accumulation time, constant potential, linearity ranges and calculated LOD obtained from the Si-gel/CPE were compared with other modified electrodes. As can be seen from Table 1, the previous studies showed insignificant influence of constant potential on the preconcentration step while our study demonstrated it as an important factor for the ASDPV. The LOD of proposed method was lower than the compared modified electrodes. It could be concluded that the Si-gel/CPE had a significant effect on the ASDPV for the determination of TA. In addition, the preparation of the proposed electrode is simpler and easier than those compared in the Table 1.

Table1. Comparison of the efficiency of some modified electrodes used in the electrocatalysis of TA

Electrode	Constant potential	Accumulation time (s)	Limit of detection (10^{-6}×mol l^{-1})	Dynamic range (10^{-6}×mol l^{-1})	Reference
Multi wall carbon nanotubes modified GCE	-	300	0.1	0.4-200	[11]
AHMP-AuNPs[1]	-	-	0.02	0.05-1	[12]
Porous pseudo-carbon paste electrode	-	100	0.01	0.02-1	[13]
Si-gel/CPE	-0.3	240	0.0003	0.001-1	This work

[1] 4-amino-6-hydroxy-2-mercaptopyrimidine capped gold nanoparticles (AHMP-AuNPs) in aqueous medium immobilized on indium tin oxide (ITO) electrode modified with (3 – mercaptopropyl)trimethoxysilane (MPTS) sol–gel.

3.3. Interferences studies

Si-gel/CPE showed a remarkable selectivity towards TA oxidation by ASDPV. The response for some metal cations: Cd^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+} Cr^{2+} K^+ ,Na^+; anions Cl^-, CO_3^{2-}, HCO_3^- as well as some organic compounds: tartaric acid, oxalic acid and citric acid, glucose at the same concentration 0.001 M in the absence of TA, was not detectable. In the presence of TA, the results show that the tolerable concentration ratios with respect to 0.5 μM TA are 200-fold for K^+, Na^+; 50-fold for Mg^{2+}, Ca^{2+} ; 20-fold for Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}; 15-fold for Cu^{2+}, Cd^{2+} and in presence of 80-fold of tartaric acid, 60-fold oxalic acid, 50-fold for ascorbic acid and citric acid, 100-fold of glucose, 200-fold for Cl^-, CO_3^{2-}, HCO_3^- the determination gives an error less than ±5.0%. In comparison with some studies before [13, 14], our results showed the higher anti-interferences ability. In our study, ascorbic acid can be demonstrated as the main organic interference species for the determination of TA in the analysis of some commercial wine, juice, vegetables using the novel method described above. The interference arises from the overlapping of the oxidation waves of both ascorbic acid and TA. This problem can be overcome by submitting the samples to a pretreatment with the enzyme ascorbate oxidase to eliminate the ascorbic acid before analysis as reported in the literature [29]. Besides, the ascorbic acid can be readily destroyed by stirring an aliquot of the sample in the presence of thin slices of the cucumber mesocarp which is rich in ascorbate oxidase [30].

3.4. Application in the real samples

The method was successfully applied to some food samples and the river water sample in Labe River, Pardubice, Czech Republic. The results confirmed that the TA measurements performed by the novel method were in good agreement with those obtained from the standard spectroscopic method [25] (Table 2). The accuracy of the method was also verified by recovering studies by the addition of standard TA solutions to the samples. Recoveries of 95 - 115% were obtained in this study.

Table 2. Tannic acid contents in some samples using Si-gel/CPE and spectroscopic method (n = 5).

Sample	Content of tannic acid in mg l^{-1} ± standard deviation	
	Proposed method	Reference method
White wine	21.1 ± 0.08	20.24 ± 0.07
Fruit juice	5.75 ± 0.07	5.65 ± 0.07
River water	0.67 ± 0.05	0.57 ± 0.06
Black tea[1]	0.53 ± 0.03	0.51 ± 0.02

[1] results expressed in mg g^{-1}

4. CONCLUSION

In this study, the electrochemical determination of TA on the surface of Si-gel/CPE by ASDPV was firstly investigated. This new kind of electrochemical sensor is proved to be of high sensitivity, excellent selectivity, reproducibility and stability. Although, the mechanism for the increased reactivity of the Si-gel towards TA is not entirely clear at present, it was shown that Si-gel/CPE remarkably enhanced the oxidation peak current of TA comparing with the unmodified CPE. The proposed method was successfully applied in the real samples. The detection limit of TA was estimated to be 0.3×10^{-9} mol l^{-1} in this work.

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