



# Advanced electrochemical platform for simple and rapid quantification of tannic acid in beverages using batch injection analysis with amperometric detection



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## ABSTRACT

In this work, an advanced electrochemical platform was developed for the simple, rapid and sensitive determination of the polyphenolic compound tannic acid in various beverages using the combination of batch injection analysis with amperometric detection on a screen-printed carbon electrode. Several experimental parameters (pH of supporting electrolyte, detection potential, dispensing rate, injected volume, stirring) were consistently evaluated. The most favorable analytical performance in terms of sensitivity, selectivity, repeatability and sampling frequency was obtained in Britton-Robinson buffer pH 5.0 at a detection potential of +0.6 V vs. Ag/AgCl, a dispensing rate of 204  $\mu\text{L/s}$  and an injected volume of 80  $\mu\text{L}$  under stirring condition (1500 r.p.m.). The presented platform has advantages for routine analysis including portable and small-scale experimental setup, low sample consumption ( $\sim 100 \mu\text{L}$ ), simple sample preparation (dilution in supporting electrolyte), high sampling frequency (180 injections per hour), low limit of detection (80 nM) and suitable precision (RSD = 4.2% for 10  $\mu\text{M}$  tannic acid,  $n = 20$ ). The applicability of the method was verified by analyzing several beverage samples (tea, wine) in spike-recovery assay with the recovery values for tannic acid ranging from 94 to 101 %.

## 1. Introduction

Phenolic compounds, ubiquitous in plants, are an essential part of the human diet and are of considerable interest for their antioxidant properties and potential beneficial health effects [1]. The average daily intake of dietary polyphenols is approximately 1 g per person [2]; the main sources are beverages, fruits and, to a lesser extent, vegetables and legumes. Among other things, tannic acid (TA) is one of the most famous representatives of the natural polyphenolic compound, which can be found in practically all typical beverages, including wine, beer, coffee, black and white tea [3]. It is a hydrolysable amphiphilic tannin derivative of gallic acid with a relatively high molecular weight ( $1700 \text{ g mol}^{-1}$ ) containing ten galloyl (3,4,5-trihydroxyphenyl) groups surrounding the glucose center [4]. TA is considered as a food additive (code number E-181) with the roles of clarifying agent, flavor adjunct and flavoring agent [5,6]. Its unique properties come from its pinwheel structure, which makes many phenol groups accessible for interactions with metals, ions, polymers and proteins [7]. For example, due to strong interactions with proteins,

tannins are often added to beers to reduce the protein content that causes the opacity of the beverage [8]. The rancid and bitter taste in red wines can be directly related to the presence of TA and comes from the grape skin, stone and stems as well as aging in oak casks. The "unpleasant" taste softens with age and becomes an indispensable element of the wine storage potential [9]. Accordingly, TA content can be regarded as a kind of standard for the quality assessment of beverages. Furthermore, TA amounts have also been quantified in wastewater discharged from coir and cork process, plant medicine, paper and leather industries [10]. Its high doses have been demonstrated to be toxic with serious effect on human health, causing vomiting, constipation, abdominal pain, and liver damage [3]. Due to its wide range of applications, precise and accurate determination of TA is of high interest not only in the food industry, but also in the medical and environmental fields. Accordingly, there is a growing need for the development of facile and reliable analytical methods for simple, rapid and reliable detection and quantification of TA in different matrices.

The determination of tannins, especially TA, has been frequently carried out by protein precipitation [11], gravimetry [12], chemilumi-

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nescence [6,13–15], spectrophotometry [8], fluorimetry [16,17], colorimetry [4,18], high-performance liquid chromatography with coulometric detection [19], ultra-high performance liquid chromatography with tandem mass spectrometry [20] and resonance Rayleigh scattering [21]. Despite the high sensitivity and low limits of detection, the corresponding analysis are often laborious and time-consuming including complicated sample preparation steps and the usage of large volumes of toxic reagents. In addition, the respective analytical procedures generally require high instrumental and analysis costs that may not be available in most laboratories for routine analysis.

Based on the chemical structure of TA, it is obvious that it undergoes electrochemical oxidation. For this reason, electroanalytical methods can be favorably used for monitoring of TA concentration due to their rapid response, operational simplicity, high sensitivity, accuracy, applicability even in non-transparent (turbid) and colored mediums. Being “environmentally friendly”, modern electroanalyses use materials, solvents and techniques in accordance with the principles of *Green Analytical Chemistry* [22]. Moreover, during the last two decades, the electroanalytical approaches are becoming more oriented towards the development of electroanalytical methodologies with miniaturized systems making them suitable for on-site investigations in many fields (e.g., biomedical, food safety, etc.) [23]. So far, electrochemical examinations, based on the different chemical modifications of  $sp^2$ -hybridized carbonaceous electrode materials such as glassy carbon [24–26], carbon paste [27–30] and graphite [31,32], have mainly been reported for the determination of TA in different samples. Typically, the modifiers such as carbon-based nanosized materials [26,28], polymer material [27] and various composite films [24,25], in some cases synthesized in-house, were employed, which make the particular modification procedures often multi-step, complex and tedious. Although the phenolic species can be easily oxidized on solid electrodes, bare electrodes from conventional materials (glassy carbon, Pt, Au) have rarely been used for voltammetric determination of these compounds. As a result of the production of the phenoxy radical and its subsequent reaction with phenol, a polymeric adherent film is strongly deposited on the electrode surface, which prevents further electron transfer and causes electrode fouling [33].

The implementation of automated analytical systems in electroanalysis, namely flow injection analysis (FIA) and batch injection analysis (BIA), can provide several additional improvements such as increased analytical throughput, reduction of reagent consumption, and minimization of waste generation. Moreover, it significantly decreases problems with electrode passivation [33–37]. An advantage over FIA is that BIA eliminates some issues common to flow systems, such as the use of pumps or valves and the disposal of reagent/carrier solutions [38]. The operation of the BIA system involves injecting small volumes of sample through a micropipette tip directly on the working electrode surface, which is immersed in a large volume of supporting electrolyte. The working electrode remains immersed in the blank solution and when the sample is injected, it is immediately diluted in the electrolyte after a transient signal is obtained [38–42]. It is important to highlight the fact that the usage of electrochemical sensors in non-stationary systems such as BIA and FIA can represent a very popular powerful tool to perform rapid and sensitive analysis. In this context, we found that the usage of the BIA system for the electrochemical screening of polyphenolic compounds, particularly TA, could be a very promising platform, which eliminates the issue of formations of polymeric adherent film on unmodified carbon electrode surfaces. The washing-out effect of the injected sample during stirring of the analyzed solution in the BIA cell supports the prevention of electrode passivation by the unwanted adsorption process of TA and its oxidation products.

Based on these facts, this work presents for the first time an unmodified commercially available screen-printed carbon electrode in tandem with a BIA system with amperometric detection (BIA-AMP) for simple, rapid and sensitive determination of TA. The special attention

was paid to the optimization of experimental parameters for the BIA-AMP method (detection potential, injection volume, dispersing rate etc.) and assessment of the main analytical features (linear concentration range, linearity, limit of detection and repeatability). The proposed methodology was applied to the determination of TA in wine and tea samples, and the successful accuracy was confirmed by the spike-recovery assay.

## 2. Experimental

### 2.1. Apparatus

Electrochemical measurements were accomplished using an AUTO-LAB PGSTAT101 (Metrohm Autolab B.V., The Netherlands) connected to a PC and controlled by NOVA software (version 1.11). Electrochemical experiments were realized on commercially available screen-printed carbon electrodes (SPCE, DRP-11L; Metrohm Dropsens, Spain) designed for the BIA setup. The body of the SPCE was made of a ceramic substrate (dimensions: L 33 × W 10 × H 0.5 mm), on which a carbon working electrode (diameter of 4 mm), a silver/silver chloride pseudoreference electrode, and a carbon auxiliary electrode are placed in the middle. This electrode arrangement is only compatible with aqueous systems, as the carbon ink used to print the SPCE could react with non-aqueous solvents. In addition, SPCEs are stable at temperatures up to 50 °C, and higher temperatures can cause problems with electrode stability due to softening of the polymer used. BIA-AMP measurements were carried out in commercial BIA-SPE cell designed for a maximum volume of 80 mL and programmable with electronic micropipettes P200M (20 – 200  $\mu$ L) using a 200  $\mu$ L DIAMOND® tips. The stirring of the analyzed solution was regulated by a BIA-STIR stirrer with a different adjustable stirring level of 500 r.p.m. (speed mode 1); 1500 r.p.m. (speed mode 2) and 3000 r.p.m. (speed mode 3). The distance between the working electrode surface of SPCE and the DIAMOND® tip was approximately 2 mm. All items for the BIA system, including the SPCE package, electrochemical cell, stirrer, electronic micropipettes, and other components, were purchased from Metrohm DropSens (Spain). The pH measurements were realized with a pHenomenal® pH 1100 L meter (VWR, Slovakia) with a combined glass-reference electrode.

### 2.2. Chemicals

All chemicals and reagents such as analyte TA, redox indicator [Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>], KCl and selected interfering species were analytically pure and were bought from Sigma Aldrich (Slovakia) or Centralchem (Slovakia). Aqueous solutions were prepared in deionized water with the resistivity higher than 18 M $\Omega$ cm. A 1 mM stock solution of TA was firstly prepared by dissolving an appropriate amount of certified reference material (Sigma Aldrich, Slovakia) in 20 mL of deionized water and then quantitatively transferred into a 50 mL volumetric flask. This solution was prepared daily to avoid problems with its lower stability, which was noticed over several days by a gradual decrease in the amperometric responses of the 10  $\mu$ M TA working solution (the decline after 3 days was 50%). Working solution and individual calibration solutions of TA were prepared freshly by diluting a suitable volume of 1 mM stock solution in a 10 mL volumetric flask with supporting electrolyte. Britton-Robinson (BR) buffer, composing of a mixture of H<sub>3</sub>BO<sub>3</sub>, CH<sub>3</sub>COOH and H<sub>3</sub>PO<sub>4</sub> (each compound at a concentration of 0.04 M), was used as the supporting electrolyte. Various pH values were adjusted by adding 0.2 M NaOH until a BR buffer with an appropriate pH value was prepared. For the initial study of the electroactive surface area of the SPCE, a redox indicator of 1 mM [Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>] in 0.1 M KCl was prepared by dissolving a specific amount in 30 mL of deionized water and then filled up with deionized water to ring the graduation mark of a 50 mL volumetric flask.

### 2.3. Measurements procedures

In a preliminary study, differential pulse voltammetry (DPV) and amperometry (AMP) were applied to find an appropriate detection technique with respect to the sensitivity, repeatability and selectivity of the analytical signal of TA. Cyclic voltammetry was executed to evaluate the electroactive surface area of the SPCE used, analyzing the redox indicator 1 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> in 0.1 M KCl (Fig. S1A, Supplementary Material). In this context, the average value of the electroactive surface area for three independent SPCEs (from the same package) was calculated to approximately 9.00 mm<sup>2</sup> (from the anodic dependence 8.95 mm<sup>2</sup> and from the cathodic dependence 9.1 mm<sup>2</sup>) with relative standard deviation for the anodic and cathodic current response RSD<sub>anodic</sub> of 4.3% and RSD<sub>cathodic</sub> of 4.5%, respectively, according to the Randles-Sevcik equation (Fig. S1B, Supplementary Material). The closer specifics of the SPCE are given in section 2.1. Apparatus. All measurements were carried out at laboratory temperature, in the presence of dissolved oxygen and without previous electrochemical pretreatment of the SPCE (only a simple cleaning of the surface by deionized water from a syringe at the beginning of a specific procedure and before changing the analyzed solution). During BIA-AMP measurements, the SPCE was always immersed in 30 mL of supporting electrolyte. In the case of optimization of the detection potential and the choice of the supporting electrolyte, background correction (based on the “moving average” function in the NOVA software) was required to eliminate the capacitive current at higher applied potentials and for a more convenient comparison of the recorded DP voltammograms. The moving average method in electroanalysis is very effective when the electrochemical signals appear as shoulders on the steep sides of the voltammograms/amperegrams, and this method is able to reduce the background current by almost 99%. OriginPro 8.0 (OriginLab, USA) was used to statistically analyze the obtained results and the relevant results (slope and intercept) were evaluated in the 95% confidence interval. The limit of detection (LOD) was calculated using the following equation (Eq. (1)):

$$LOD = 3 \times s_a/b \quad (1)$$

where  $s_a$  is standard deviation of intercept, and  $b$  is slope of the particular calibration curve.

### 2.4. Preparation of wine and tea samples

In this study, one red wine sample (*JP. Chenet Cabernet Syrah*) and two tea samples (*Lloyd Fruit Tea grog tea plum*, *Lord Nelson English breakfast black tea*) were analyzed by BIA-AMP method with SPCE. These samples were obtained from different local groceries in Bratislava (Slovakia). The wine sample was treated by a simple 100-fold dilution in deionized water to create a stock sample solution. Subsequently, 1 mL of this solution was added to a 10 mL volumetric flask and filled with supporting electrolyte. A very similar procedure was applied to the preparation of tea samples, but with the initial steps, where one tea bag was steeped in 250 mL of boiled deionized water. Afterwards, 1 mL of tea extract was added to a 100 mL volumetric flask and filled up with deionized water to prepare the stock solution of tea sample. The working solution of the tea sample was prepared by simple dilution of 1 mL of the stock solution in a 10 mL volumetric flask with supporting electrolyte. The TA content in these samples was determined by a standard addition method and the solutions were prepared according to the following procedure: 1 mL aliquot of stock sample solution was added to the four single 10 mL volumetric flasks. Subsequently, corresponding volumes of 100 µL, 150 µL and 200 µL of 0.1 mM TA standard solution were placed in the second, third and fourth volumetric flask, respectively and the entire volume of these flasks were filled up with supporting electrolyte.

## 3. Results and discussion

### 3.1. Selection of appropriate electrochemical technique

One of the initial steps before starting method development was to find an appropriate electrochemical technique providing a sensitive and repeatable analytical signal of TA. In this regard, we decided to study in detail the analytical signal of TA on SPCE using AMP and DPV. Based on this fact, the intensity of the analytical responses of TA and their repeatability were investigated by performing 10 subsequent DPV measurements of 100 µM TA in BR pH 2.0 in a stationary arrangement and 10 successive injections of 100 µM TA in BR buffer pH 2.0 at a detection potential of +0.8 V using the BIA-AMP system. The detection potential value of +0.8 V was selected based on the peak potential value for 100 µM TA registered in the previous DP voltammogram on the same SPCE. As shown in Fig. 1, the electrochemical activity of TA was accompanied by substantial adsorption on the working surface of the SPCE, leading to a decrease in the recorded analytical responses of TA (most dominant in the first 5 DPV scans and BIA-AMP injections), regardless of the electrochemical technique used. However, the application of the BIA-AMP method (Fig. 1A and 1C) provided a higher current response of TA (approximately 5-times higher) compared to the case when DPV was used as the detection technique (Fig. 1B and 1D). The particular RSD values were 40.3% and 78.8% (in the case of 1st peak) for BIA-AMP and DPV, respectively, which clearly represented the favorable repeatability of analytical responses of TA for BIA-AMP. Additionally, this effect can be greatly enhanced by stirring of the analyzed solution in the BIA-AMP system during the measurement, leading to a faster washing-out effect of the injected sample, which prevents the undesirable adsorption process of the phenolic compound TA and its oxidation products on the working electrode surface.

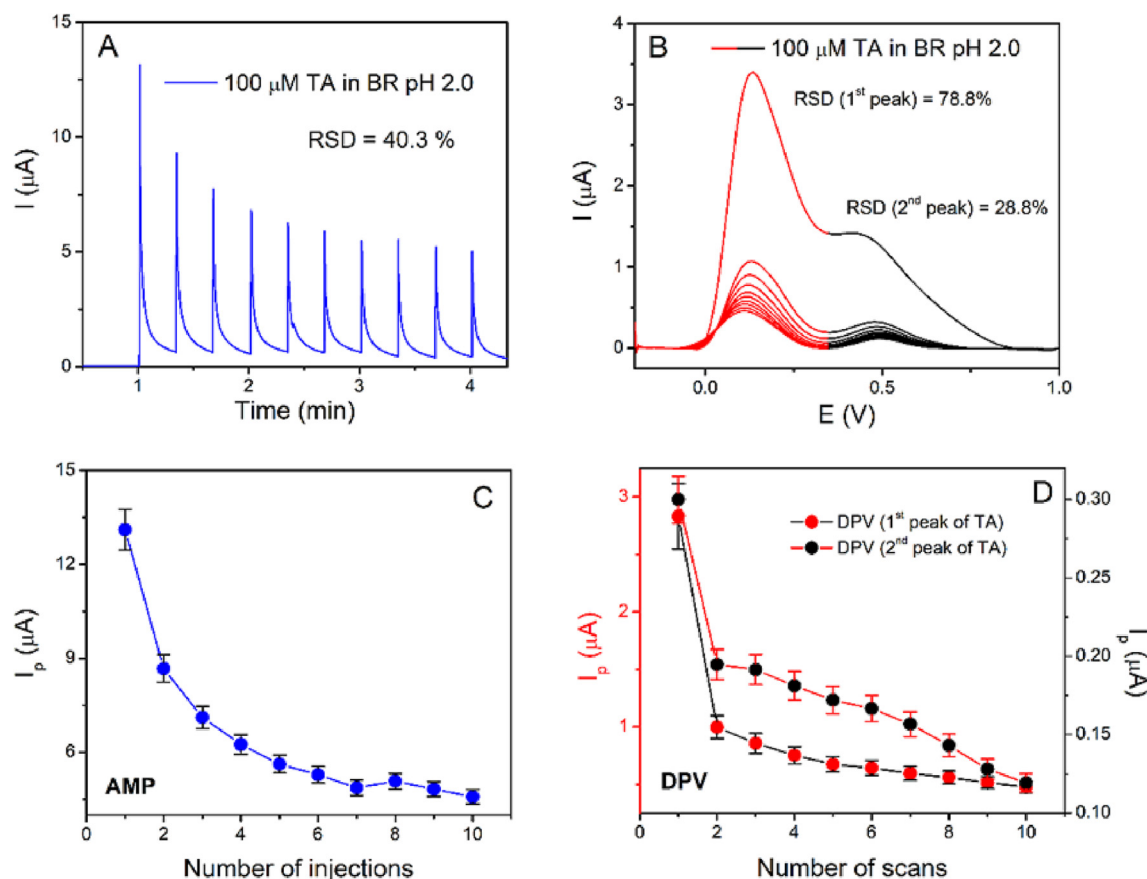
Since the electrochemical activity of polyphenolic compounds is highly dependent on the pH of the supporting medium, the next step was aimed at exploring the effect of the pH of the supporting electrolyte on the recorded analytical response of TA measured by DPV and BIA-AMP. For the individual DPV measurements of 100 µM TA at different pH values of BR buffer, a new SPCE was always used. In the case of BIA-AMP method, SPCEs were also used in hydrodynamic measurement mode. The detection potential in the BIA-AMP arrangement was set to +0.6 V vs. Ag/AgCl which was chosen based on the results from the hydrodynamic voltammogram (marked by blue colour in Fig. S2, Supplementary Material). Although the highest amperometric response of TA was recorded at a potential of +0.7 V, a potential of +0.6 V was selected as preferable, due to possible undesirable interferences of potentially electroactive species at higher potentials in real samples. In the case of using DPV as a detection technique, TA provided two oxidation peaks, the first distinctive at +0.28 V and the second “tailed” at +0.60 V in BR buffer pH 2.0, and with increasing pH, the peak potentials ( $E_p$ ) were slightly shifted to more negative potentials according to equations (Eq. (2) and Eq. (3) (Fig. S3A and S3B, Supplementary Material):

$$E_p(\text{V}) = 0.373 - 0.052 \times \text{pHR}^2 = 0.9633 \text{ for } 1^{\text{st}} \text{ oxidation peak at } +0.28\text{V} \quad (2)$$

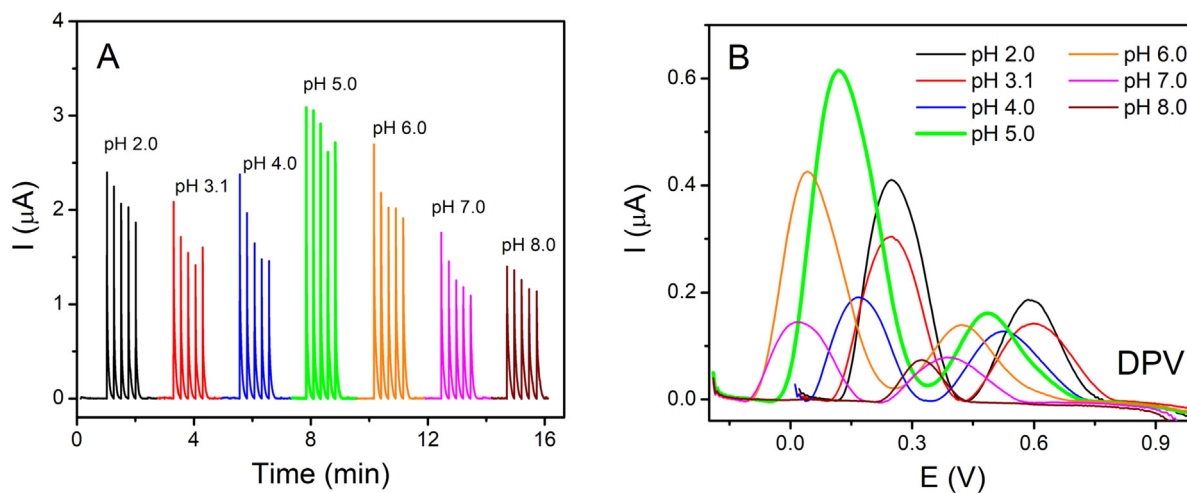
$$E_p(\text{V}) = 0.710 - 0.047 \times \text{pHR}^2 = 0.9671 \text{ for } 2^{\text{nd}} \text{ oxidation peak at } +0.60\text{V} \quad (3)$$

Obviously, the values of the slopes (0.052 and 0.047 V/pH) suggest the fact that the number of protons is equal to the electron transfer number in the electrochemical reaction of TA on SPCE, which is in good agreement with the results obtained on other working electrodes reported in previous publications [24,26,27].

Fig. 2 demonstrates a very similar trend in the electrochemical activity of TA on SPCE using both detection techniques, starting with



**Fig. 1.** Ten successive injections (scans) of 100  $\mu\text{M}$  TA in BR buffer pH 2.0 recorded with BIA-AMP (DPV) on SPCE (A, B); Amperometric/voltammetric responses of individual injections/scans (C, D). Experimental conditions: detection potential: +0.8 V, injected volume: 40  $\mu\text{L}$ , dispensing rate: 204  $\mu\text{L}/\text{s}$  (A); modulation amplitude: 100 mV, modulation time: 100 ms (B); without stirring between injections/scans (A, B).



**Fig. 2.** Five successive BIA-AMP recordings of 100  $\mu\text{M}$  TA in BR buffer at different pH values between 2.0 and 8.0 on SPCE; Experimental conditions for BIA-AMP: detection potential: +0.6 V, injected volume: 40  $\mu\text{L}$ , dispensing rate: 204  $\mu\text{L}/\text{s}$ , without stirring (A); Baseline corrected DP voltammograms (2nd scan) of 100  $\mu\text{M}$  TA in BR buffer at different pH values between 2.0 and 8.0 on SPCE in a potential range from  $-0.2$  V to +1.0 V; Experimental conditions for DPV: modulation amplitude: 100 mV, modulation time: 100 ms (B).

a decrease in the recorded amperometric or voltammetric response of TA from pH 2 to 4, followed by the most noticeable analytical signal of TA in BR buffer pH 5.0, which was selected as favorable pH of the supporting electrolyte for all subsequent measurements. Afterwards, the electrochemical activity of TA was diminished markedly from pH 5

to 8, even the 1st oxidation peak of TA disappeared at pH 8. This phenomenon is related to the proton participating in the electrochemical reaction of TA. Besides, the electrochemical oxidation of TA in a more basic environment is demanding owing to the lack of a proton involving in the electrode reaction of analyte [24]. We concluded that

amperometry in a hydrodynamic arrangement with the BIA-AMP system could be a suitable electrochemical detection technique for TA sensing due to higher current responses of TA, better repeatability as well as the possibility of partial prevention of adsorption of TA on the working electrode surface by using external stirring of the solution during analysis.

### 3.2. Repeatability study of the BIA-AMP responses

After choosing BIA-AMP as a suitable electrochemical technique for TA sensing, a repeatability study had to be performed. This was primarily due to an undesirable memory effect causing a gradual decrease in the amperometric response of TA, which is observed in Fig. 1A and 1C. A repeatability study was carried out by performing 20 successive injections of 10  $\mu\text{M}$  TA while stirring the blank solution on the SPCE in the BIA cell (Fig. 3A). The corresponding RSD = 4.1% unambiguously demonstrated that the proposed analytical platform provided acceptable repeatability at relatively low concentration levels of TA with negligible memory effect, clearly demonstrating minimal passivation of the working electrode surface.

In general, the stirring the blank solution in the BIA cell improves analytical frequency and stabilization of the baseline by fast removing oxidation/reduction products from the surface of the working electrode, which also reduces the probability of contamination of the working electrode [36,40,43,44]. This phenomenon was also observed in the case of TA in this work, when different speeds of stirring the electrolyte in the BIA cell were applied during the measurement. As shown in Fig. 3B, stirring resulted in a faster decrease of the amperometric response of TA to the current baseline, which significantly enhanced the analytical frequency from 60 injection  $\text{h}^{-1}$  (no stirring) to 120 injection  $\text{h}^{-1}$  (stirring mode 1), 180 injection  $\text{h}^{-1}$  (stirring mode 2, marked by blue colour) and 240  $\text{h}^{-1}$  (stirring mode 3). From the achieved results, it is clear that the stirring while registering the amperometric responses of TA proportionally increased the analytical frequency by 60 injection  $\text{h}^{-1}$  in each individual mode of stirring. Although a higher stirring speed (mode 3) marginally improved the analytical frequency, it also led to an increase in noise and oscillation in the baseline current. We described a similar trend in previous paper dealing with the BIA-AMP quantification of theobromine in chocolate products [41]. For this reason, stirring mode 2 (1500 r.p.m.) was considered the most favorable for further BIA-AMP measurements.

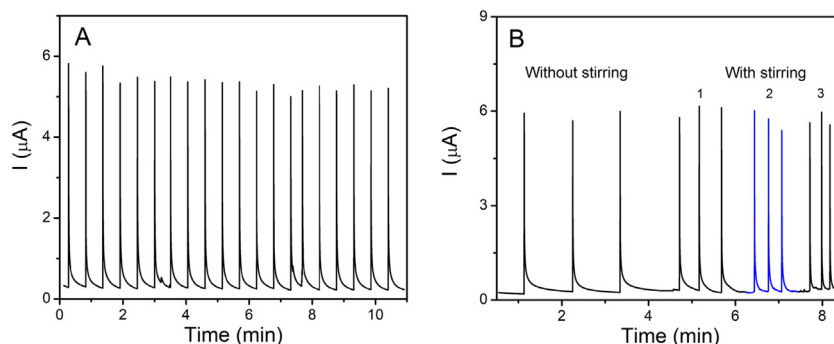
### 3.3. Optimization of experimental parameters for BIA-AMP system

The essential experimental parameters in the BIA-AMP system, which meaningfully affect the amperometric response of the electroactive substance, are the dispensing rate and the injected volume. In most

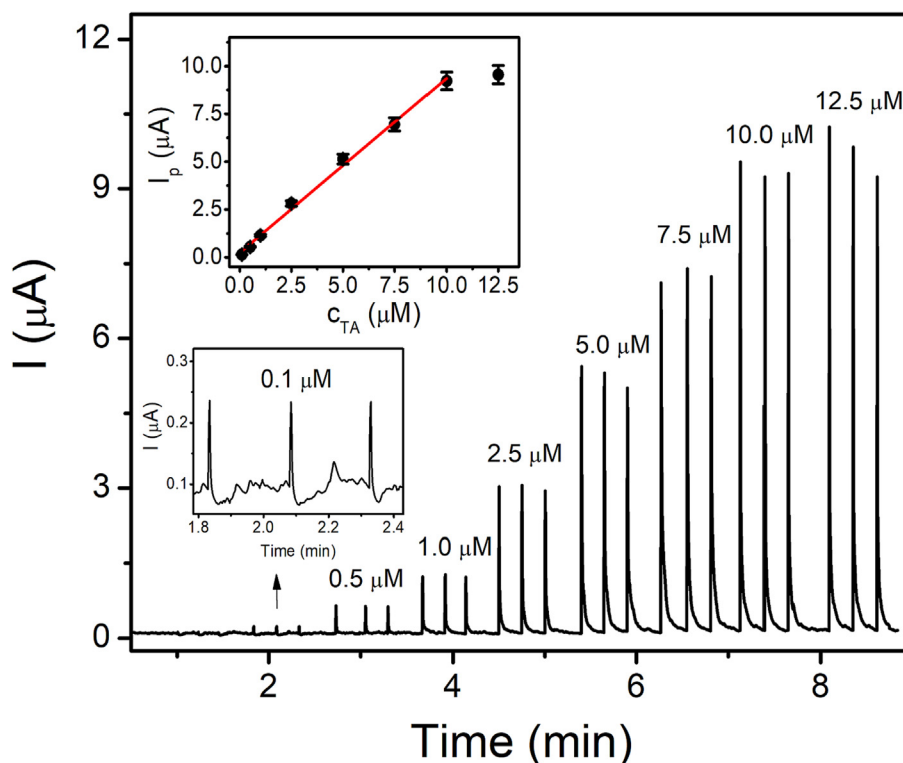
cases, with raising dispensing rate, the recorded amperometric response is higher with a faster return of the current to the baseline, which is closely related to the analytical frequency and the time of the entire analysis [36]. The effect of dispensing rate on the amperometric response of TA in BR buffer pH 5.0 on SPCE was studied in the range from 7  $\mu\text{L/s}$  to 204  $\mu\text{L/s}$ . As evident from Fig. S4 (Supplementary Material), a higher dispensing rate led to an increase in the amperometric response of TA. Moreover, it reduced the time required for the current to return to baseline. The effect of injected volume on the current response of 10  $\mu\text{M}$  TA was investigated from 20  $\mu\text{L}$  to 100  $\mu\text{L}$ . Fig. S5 (Supplementary Material) displays a noticeable increase in the amperometric response of TA with raising injection volume. Although the most intensive amperometric response was recorded at 100  $\mu\text{L}$ , we concluded that 80  $\mu\text{L}$  represented a reasonable value due to the better repeatability of current responses of TA. Lower values of the injected volume may affect the decline of the undesirable memory effect caused by the adsorption of TA on the SPCE surface. Based on this study, a dispensing rate of 204  $\mu\text{L/s}$  (marked by blue colour in Fig. S4) and an injected volume of 80  $\mu\text{L}$  (marked by blue colour in Fig. S5) were selected as reasonable values for further BIA-AMP measurements.

### 3.4. Analytical performance assessment

As part of the development of a novel analytical method, it is necessary to investigate the range of concentrations in which the analyte signal is linear. It means the concentration range in which the sensitivity of the detector is constant and the coefficient of determination is  $\geq 0.99$ . Fig. 4 presents the BIA-AMP responses obtained by triplicate injections of 80  $\mu\text{L}$  working solution of TA in BR buffer pH 5.0 on SPCE in a relatively narrow concentration range from 0.1  $\mu\text{M}$  to 12.5  $\mu\text{M}$  in ascending mode. The amperometric current response linearly increased with increasing concentration in the range from 0.1  $\mu\text{M}$  to 10  $\mu\text{M}$ . At a higher concentration, the current response of TA was not linearly sensitive to the change in TA concentration, which could be explained by the saturation of the working electrode surface. However, in this step, it should be advocated that the TA content in beverages is relatively low [26,29,31]. Therefore, the main attention was focused on the lower concentration levels of TA and additional investigations for “spreading” of the linear range were not conducted. This phenomenon is in contrast to the results obtained in the repeatability study, in which the analytical responses of 20 successive injections of 10  $\mu\text{M}$  TA were sufficiently repeatable. In this context, there are several articles in the scientific literature in which a similar issue is discussed in terms of the construction of the calibration curve [45]. The observed negative memory effect could be partially eliminated by applying a cleaning potential using multi-pulse amperometry



**Fig. 3.** BIA-AMP recordings for 20 successive injections of TA working solution, with stirring at speed mode 2 on SPCE (A). BIA-AMP responses of TA acquired without stirring and with various speed of stirring of the electrolyte in the BIA cell (speed mode 1: 500 r.p.m., speed mode 2: 1500 r.p.m., speed mode 3: 3000 r.p.m.) on SPCE ( $n = 3$ ) (B). Experimental conditions: TA concentration: 10  $\mu\text{M}$ , electrolyte: BR buffer pH 5.0, detection potential: +0.6 V, injected volume: 40  $\mu\text{L}$ , dispensing rate: 204  $\mu\text{L/s}$  (A, B).



**Fig. 4.** BIA-AMP recordings for triplicate injection of TA working solutions in the concentration range from 0.1  $\mu\text{M}$  to 12.5  $\mu\text{M}$  and the corresponding calibration curve (inset). Experimental conditions: electrolyte: BR buffer pH 5.0, detection potential: +0.6 V, injected volume: 80  $\mu\text{L}$ , dispensing rate: 204  $\mu\text{L/s}$ , with stirring of the electrolyte solution (1500 r.p.m.).

(MPA) [46,47], which is, however, still unavailable in the NOVA software. Totally, a linear concentration range from 0.1  $\mu\text{M}$  to 10  $\mu\text{M}$  TA was observed under appropriate experimental conditions (inset of Fig. 4, also with 12.5  $\mu\text{M}$  TA as an outlier) without using a cleaning/pretreatment step of the working electrode, only stirring of the electrolyte in the BIA cell. The constructed calibration curve yielded good linearity with a coefficient of determination  $R^2 = 0.9953$ . Other analytical parameters acquired from the calibration curve (sensitivity, LOD, repeatability) are given in Table 1.

### 3.5. Interference study

The influence of potential interfering compounds on the BIA-AMP determination of TA was investigated to verify the sufficient selectivity of the proposed analytical protocol. Common inorganic ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) and organic compounds (oxalic acid, glucose, sucrose) were studied as potential interfering compounds. The criterion used for a substantial interference effect was a

change of 10% or more in the recorded amperometric response of the 10  $\mu\text{M}$  TA. The results showed that the tolerable concentration of the studied interferences were 100-fold of glucose, sucrose, caffeine, theophylline,  $\text{Na}^+$ , 40-fold of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , 20-fold of oxalic acid,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  compared to 10  $\mu\text{M}$  TA. Based on the obtained results it can be assumed that the proposed analytical platform appears to be sufficient selective for the determination of TA in beverages. As was previously mentioned, the presence of caffeine and theophylline in the tea samples did not affect the amperometric signal of TA owing to their high oxidation potential ( $> 1.1$  V vs. Ag/AgCl pseudoreference electrode) compared to the applied detection potential for TA of +0.6 V.

### 3.6. Real sample analysis

The practical feasibility of the proposed analytical platform was examined by determining TA in three commercial beverage samples (fruit tea, black tea, red wine; see section 2.4. Preparation of wine and tea samples) (Fig. 5). It is important to point out that tea and wine are considered the main source of antioxidants with different amount of phenolic compounds. The applied detection potential of +0.6 V was shown to be selective for distinguishing other phenolic compounds that have high reducing capacity leading to effective antioxidant power. At a detection potential higher than +0.6 V, most of these substances present in the samples can be oxidized and subsequently evaluated electrochemically [48]. Since the actual content of TA in analyzed samples was unknown, a “spike-recovery” assay was undertaken to evaluate the accuracy of the results obtained. The determined amount of TA in the analyzed samples by the herein introduced BIA-AMP method is summarized in Table 2. The results are expressed as a confidence interval with 95% probability. The quantified TA contents clearly suggest that the BIA-AMP method is suitable for the determination of TA in beverage samples such as tea and red wine.

**Table 1**

Analytical parameters of the BIA-AMP method for the determination of TA.

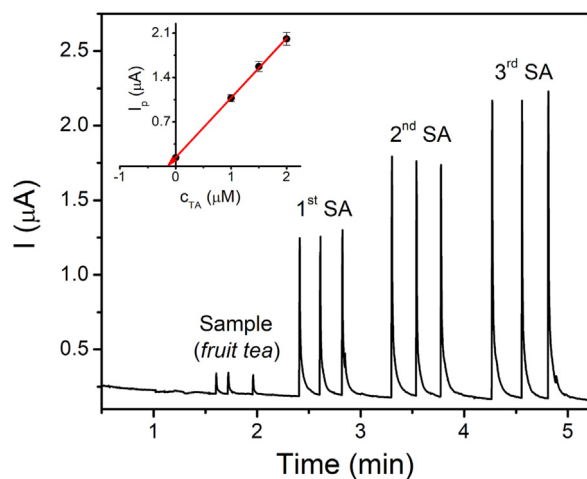
Analytical parameter	Determined value
Intercept ( $\mu\text{A}$ )	$0.2460 \pm 0.0239$
Slope (Sensitivity) ( $\mu\text{A}/\mu\text{M}$ )	$0.9110 \pm 0.0256$
Linear concentration range ( $\mu\text{M}$ )	0.1 – 10.0
Linearity $R^2$	0.9953
LOD (nM)	80
Analytical frequency*	180
Repeatability (%)**	4.2

\*number of injections per hour for 10  $\mu\text{M}$  TA (stirring mode 2).

\*\*for 20 successive amperometric responses of 10  $\mu\text{M}$  TA.

### 3.7. Comparison with other electroanalytical approaches

When comparing the analytical performance of the proposed strategy with other electrochemical sensors for the determination of TA (Table 3), it should be emphasized that only a few works presented the determination of this polyphenol using unmodified electrochemi-



**Fig. 5.** BIA-AMP recordings for a fruit tea sample with standard additions of 0.1 mM TA (1<sup>st</sup> SA, 2<sup>nd</sup> SA, 3<sup>rd</sup> SA) with corresponding graphical evaluation of TA quantification by the standard addition method (inset). Experimental conditions: electrolyte: BR buffer pH 5.0, detection potential: +0.6 V, injected volume: 80  $\mu$ L, dispensing rate: 204  $\mu$ L/s, with stirring of the electrolyte solution (1500 r.p.m.).

**Table 2**

The determined amount of TA in wine and tea samples by the standard addition method in the “spike-recovery” assay ( $n = 3$ ).

Sample	TA in sample ( $\mu$ M)	TA added ( $\mu$ M)	TA measured ( $\mu$ M)	Recovery (%)
Black tea	0.400 $\pm$ 0.018	1.0	1.310 $\pm$ 0.098	93.6
Fruit tea	0.147 $\pm$ 0.006	1.0	1.161 $\pm$ 0.054	101.1
Red wine	0.226 $\pm$ 0.010	1.5	1.711 $\pm$ 0.101	99.1

**Table 3**

Comparison of the performance of various electroanalytical approaches for the determination of TA.

Working electrode	Supporting electrolyte	Accumulation potential (V)	Accumulation time (s)	Detection technique	Linear range ( $\mu$ M)	LOD (nM)	Analyzed samples	Reference
Pre-PGE	BR, pH 4.0	-0.1	180	ASDPV	0.005 – 0.5	1.5	beverages	[31]
GE obtained from waste zinc-carbon batteries	0.1 M NaCl	-0.9	90	ASDPV	0.001 – 0.04	1.8	wines	[32]
PPCPE	BR, pH 5.5	OC conditions	100	ASLSV	0.02 – 1	10	–	[30]
PEG/CPE	BR, pH 5.0	OC conditions	60	ASDPV	0.08 – 2.1	72	beers	[27]
Si-gel/CPE	BR, pH 6.0	-0.3	240	ASDPV	0.001 – 1	0.3	wine, juice, tea, water	[29]
SWCNTs/GCE	PB, pH 4.0	OC conditions	180	ASDPV	0.05 – 1	8	tea, beer	[26]
PrTu-GCE	BR, pH 2.0	–	–	DPV	2 – 42	600	juice, tea	[24]
NiHCF-AFCNT/GCE	PB, pH 7.0	–	–	DPV	10 – 170	1000	–	[25]
Nd <sub>2</sub> O <sub>3</sub> @GP	PB, pH 7.6	–	–	CV	5 – 200	700	–	[49]
SPCE	BR, pH 5.0	–	–	BIA-AMP	0.1 – 10	80	tea, wine	This work

Abbreviations: ASDPV – anodic stripping differential pulse voltammetry, ASLSV – anodic stripping linear sweep voltammetry, BIA-AMP – batch injection analysis with amperometric determination, BR – Britton-Robinson buffer, CV – cyclic voltammetry, DPV – differential pulse voltammetry, GE – graphite electrode, GP – graphite powder, NiHCF-AFCNT/GCE – glassy carbon electrode modified with nanocomposite film of nickel hexacyanoferrate electrodeposited onto amino functionalized multiwalled carbon nanotubes, OC – open-circuit, PB – phosphate buffer, PEG/CPE – carbon paste electrode modified with poly(ethylene glycol), PPCPE – porous pseudo-carbon paste electrode, Pre-PGE – pretreated pencil graphite electrode, PrTu-GCE – glassy carbon electrode modified with 1-benzoyl-3-(pyrrolidine) thiourea, Si-gel/CPE – silica gel modified carbon paste electrode, SPCE – screen-printed carbon electrode, SWCNTs/GCE – glassy carbon electrode modified with single-wall carbon nanotubes.

cal sensors [30–32]. Furthermore, most of the published papers have also paid the promoting effect of adsorption on the carbonaceous working electrode surfaces and the utilization of this feature for the enhancement of analytical sensitivity, leading to lower LODs. For instance, Xu *et al.*, reported a detailed investigation for the determination of TA by anodic stripping voltammetry and showed clear advantages of porous structure of electrochemical sensors over modified ones. The porous pseudo-carbon paste electrode presented a LOD of 10 nM, which was 10-times lower than that of using carbon paste electrode (CPE) and about 5-times lower than that of either polypyrrole modified CPE or SBA-15 modified CPE [30].

The coupling of a pretreated pencil graphite electrode and anodic stripping differential pulse voltammetry (ASDPV) after an accumulation step for 180 s was utilized for the sensitive determination of TA in beverages with a LOD of 1.5 nM [31]. The sensitivity in ppb order (LOD of 1.8 nM) was also reached in the determination of TA in commercially available Merlot wines using a tandem ASDPV and a graphite electrode obtained from waste zinc-carbon batteries [32]. Considering the tandem of modified electrodes and stripping techniques, as expected, the two reported methods offered LODs at nanomolar levels [26,29] and were significantly lower than the LOD presented in this work. On the contrary, it is worth noting that the sensitivity accomplished by the herein declared protocol is improved compared to those achieved by DPV using a glassy carbon electrode (GCE) modified with either a modified by 1-benzoyl-3-(pyrrolidine) thiourea [24] or a nickel hexacyanoferrate nanocomposite film and functional MWCNTs [25], also using Nd<sub>2</sub>O<sub>3</sub> modified graphite electrode [49] and comparable to CPE modified with poly(ethylene glycol) [27]. Furthermore, the implementation of the BIA arrangement enabled fast, high-throughput and automated screening of polyphenol content. Compared to previously reported electrochemical procedures, the presented BIA-AMP system does not require multi-step and complex electrode modifications; moreover, problems with electrode fouling are minimized by measuring in a non-stationary system. Such characteristics also make this tandem a very promising tool for the determination of antioxidant activity in routine applications [50,51].

## 4. Conclusions

In this work, an advanced analytical platform, based on the combination of batch injection analysis with amperometric detection on a screen-printed carbon electrode, is demonstrated for the first time

for the simple, rapid and sensitive determination of TA in beverages. Compared to other analytical methods such as liquid chromatography, this modern electroanalytical protocol has many advantages, especially in the lower consumption of toxic reagents and samples, simplicity (only a simple dilution in the supporting electrolyte), price, and also in a higher analytical frequency (180 injections per hour). The herein introduced platform, with a LOD of 80 nM for TA, has the potential to be utilized as a fair analytical protocol for the quantification of TA in food quality control. Furthermore, it meets the requirement of the principle of *Green Analytical Chemistry* such as no organic solvent use, *in-situ* measurements, portability as well as a direct analytical procedure without laborious sample pretreatment step, automation and miniaturization. An achievable improvement of this protocol could lie in the use of multi-pulse amperometry as a detection technique, which can avoid considerable issue with the adsorption of polyphenolic compounds, especially if sp<sup>2</sup>-hybridized carbon (graphite, glassy carbon) could be used as the working electrode material.

### CRedit authorship contribution statement

**Marek Haššo:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Visualization. **Olha Sarakhman:** Writing – original draft, Methodology, Investigation, Resources, Data curation. **Slađana Đurđić:** Methodology, Investigation, Data curation, Visualization, Writing – review & editing. **Dalibor Stanković:** Methodology, Supervision, Writing – review & editing, Project administration. **Lubomír Švorc:** Conceptualization, Supervision, Methodology, Validation, Writing – review & editing, Project administration.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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