

Please cite the Published Version

Pierini, GD, Maccio, SA, Robledo, SN, Ferrari, AGM, Banks, CE, Fernández, H and Zon, MA (2020) Screen-printed electrochemical-based sensor for taxifolin determination in edible peanut oils. *Microchemical Journal*, 159. ISSN 0026-265X

DOI: <https://doi.org/10.1016/j.microc.2020.105442>

Publisher: Elsevier

Version: Published Version

Downloaded from: <https://e-space.mmu.ac.uk/627977/>

Usage rights:  [Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/)

Additional Information: This is an Author Accepted Manuscript of an article published in *Microchemical Journal*.

Enquiries:

If you have questions about this document, contact openresearch@mmu.ac.uk. Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)

Journal Pre-proofs

Screen-printed electrochemical-based sensor for taxifolin determination in edible peanut oils

Gastón Darío Pierini, Sabrina Antonella Maccio, Sebastián Noel Robledo, Alejandro García-Miranda Ferrari, Craig Edward Banks, Héctor Fernández, María Alicia Zon

PII: S0026-265X(20)31863-4
DOI: <https://doi.org/10.1016/j.microc.2020.105442>
Reference: MICROC 105442

To appear in: *Microchemical Journal*

Received Date: 4 June 2020
Revised Date: 19 August 2020
Accepted Date: 19 August 2020

Please cite this article as: G. Darío Pierini, S. Antonella Maccio, S. Noel Robledo, A. García-Miranda Ferrari, C. Edward Banks, H. Fernández, M. Alicia Zon, Screen-printed electrochemical-based sensor for taxifolin determination in edible peanut oils, *Microchemical Journal* (2020), doi: <https://doi.org/10.1016/j.microc.2020.105442>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Elsevier B.V. All rights reserved.



Screen-printed electrochemical-based sensor for taxifolin determination in edible peanut oils

Gastón Darío Pierini^{a*}, Sabrina Antonella Maccio^a, Sebastián Noel Robledo^{b*}, Alejandro García-Miranda Ferrari^c, Craig Edward Banks^c, Héctor Fernández^a, María Alicia Zon^a.

^a Departamento de Química, Grupo GEANA, Instituto para el Desarrollo Agroindustrial y de la Salud (IDAS), Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Agencia Postal No 3, 5800, Río Cuarto, Argentina

^b Departamento de Tecnología Química, Grupo GEANA, Instituto para el Desarrollo Agroindustrial y de la Salud (IDAS), Facultad de Ingeniería, Universidad Nacional de Río Cuarto, Agencia Postal N°3 (5800) Río Cuarto, Argentina.

^c Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK

*Corresponding Authors

E-mail addresses: gpierini@exa.unrc.edu.ar (G. D. Pierini); sabrimaccio@gmail.com (S. A. Maccio); srobledo@ing.unrc.edu.ar (S. N. Robledo); a.garcia-miranda.ferrari@mmu.ac.uk (A. García-Miranda Ferrari); c.banks@mmu.ac.uk (C. E. Banks); hfernandez@exa.unrc.edu.ar (H. Fernández); azon@exa.unrc.edu.ar (M. A. Zon)

Abstract

An electrochemical method for the determination of Taxifolin (Tx) in peanut oil samples using screen-printed electrodes (SPEs) is reported for the first time. The different electroanalytical parameters such as scan rate, supporting electrolyte, pH and accumulation step were optimized. Interference studies were also explored for the determination of Tx in presence of daidzein, quercetin, trans-resveratrol and caffeic acid. The method developed for the Tx determination exhibits a linear response in the concentration range from 0.05 to 1 μM and a limit of detection of 0.021 μM . The electrochemical detection method proposed provides a novel, quick, low-cost, reliable and portable method for the *in-situ* quality control for monitoring the protected designation of origin of the “Córdoba, Argentina, Peanuts”.

Keywords: Taxifolin; Peanut oils; Screen-printed electrodes; Electrochemical sensor.

1. Introduction

Peanut oil is an edible vegetable oil widely used due to its unique nutritional, medicinal and sanitary properties [1]. It is extracted from shelled and crushed peanuts using a variety of methods such as hydraulic pressing, expeller pressing and/or solvent extraction [2]. The chemical composition of peanut oil varies according to the geographical origin of the peanuts having triacylglycerols and their fatty acids as the major components. There are also other minor components such as free fatty acids, diacylglycerols, phospholipids, sterols, tocopherols, tocotrienols, triterpenic and aliphatic alcohols, waxes, pigments, phenolic compounds, and metals [3]. It is also important to note the presence of several phenolic compounds that have been found in peanut samples such as quercetin, isoquercetin, daidzein, trans-resveratrol, caffeic acid and taxifolin among others [4-6].

Taxifolin (3,5,7,3,4-pentahydroxy flavanone, Tx), also known as dihydroquercetin, is one of the most bioactive flavonoids. Its chemical structure is shown in Fig. 1. Tx is reported to take part of many biological processes such as inhibitory activity on three digestive enzymes [7], anti-inflammatory and anti-allergic effects on mast cells and mast cell-mediated allergic reaction [8], reduction of androgen production in leydig immature rat testis [9], decrease in cholesterol oxidation product [10], and many others that can be found in the specific literature [11]. Tx, can be naturally found in milk thistle, onions, chinese plant extracts (such as *Polygonum orientale*, *turtle jelly* and extract of *Rhizoma Smilacis Glabrae*), citrus fruits, peanuts, and others [12-17].

Commercially available Tx determination methods are mainly based on high-performance liquid chromatography (HPLC), with different detection systems such as mass spectrometry (MS) [18, 19], UV-vis [20, 21], photodiode array detector [14] or capillary electrophoresis (CE) [15, 22]. Although these methods exhibit accuracy and sensitivity, they require expensive equipments and technical expertise, high amount of reagents, time-consuming and a centralized laboratory to perform the analysis. Most of them need an internal standard which could improve the method performance (butylparaben, biochanin A), and a liquid/liquid extraction stage prior to analysis. In all these methods, the mobile phase consists of organic solvents (acetonitrile, trifluoroacetic acid, methanol, acetic acid). Moreover, the limits of detection (LOD) vary between 0.004 - 0.005 μM for mass spectrometry detection to 0.66 - 0.76 μM for other detection methods.

On the other hand, electrochemical methods offer analytical advantages such as high degree of accuracy, precision, sensitivity and selectivity, small size of equipments, low cost and easiness of sample preparation. Thus, they are good candidates as promising alternative methods to carry out the determination of Tx. At present, there are only a few reports regarding the determination of Tx by electrochemical sensors. The Tx electrochemical behavior has been studied at different pH at glassy carbon mini-electrodes (GCmE) by using cyclic, differential pulse and square wave voltammetries (CV, DPV and SWV) [23]. Ziyatdinova et al. [24] have developed an electroanalytical method to determine rutin, quercetin and Tx in pharmaceutical dosage by using CV on multi walled carbon nanotube modified glassy carbon electrodes (MWCNT-GCE). The linear concentration range (LCR) to determine Tx was from 0.52 to 210 μM and, the LOD was 0.26 μM . Y. Wu et al. [25], used an electrochemically reduced graphene oxide (ERGO) on a glassy carbon electrode (ERGO-GCE) and square wave adsorptive stripping voltammetry (SWASV) for the detection of Tx in prince's-feather fruit. They reported a LCR from 0.05 to 1.5 μM and the LOD was 0.004 μM . The electrodeposition of electrochemical reduced graphene oxide on a glassy carbon electrode (ERGO-GCE) in combination with SWASV was also reported for the Tx determination in prince's-feather fruit, exhibiting a LCR from 0.01 to 1 μM and a LOD of 0.002 μM [26]. Palladium nanoparticles supported on poly (diallyldimethylammonium chloride) (PDDA)-functionalized graphene modified GCE (PDDA-Gr-Pd-GCE) were also used for the Tx determination in *Fructus Polygoni Orientalis*, exhibiting LCR from 0.04 to 1 μM and a LOD 0.001 μM , respectively [27]. Recently, a molybdenum sulfide and nitrogen doped active carbon composite (MoS_2/ANC) modified GCE (MoS_2/ANC -GCE) sensor for the determination of Tx was reported, with a LCR from 0.001 to 1 μM and a very low LOD of 0.0003 μM , which was applied to the quantitative detection of Tx in *Fructus Polygoni Orientalis* [28]. The electrochemical methods previously described have an excellent LOD, even better than those found with HPLC-MS. However, some limitations can be mentioned such as a large volume in the electrochemical cell (10 mL or more). This implies a large reagent consumption and more waste generated. On the other hand, all of them have electrode surface modification with nanostructures, which involve several stages to obtain the final sensor (material synthesis, material characterization, preparation of modified electrodes, etc.). Furthermore, all the previously described sensors show an adsorption controlled electrode

process or an adsorption/diffusion controlled electrode process. Besides, in no case the accumulation stage was optimized using an experimental design. In addition, in all cases the electrode surface must be regenerated between each experiment, leading to time consumption. However, at so far, no electrochemical method was reported for the Tx determination in peanut samples.

In recent years, there has been a trend of increased attention to develop *in-situ* analytical methodologies outside central laboratories, such as “point of care analysis” or “decentralized analysis” [29, 30]. In this context, screen-printed electrodes (SPEs) are the basis of translating lab-based methodologies on “in-the-field” experimentation. SPEs offer great versatility, small size, low reagent consumption, low-cost and large-scale manufacture and, they are highly reproducible for single or multiple use, providing a great analytical platform to develop in real time *in-situ* sensor devices [31-33]. Several of these advantages, follow the most of the principles involved in green chemistry [34,35].

In this work, we report the results of a simple and reliable electroanalytical method to determine Tx (see its chemical structure in Fig. 1) in edible peanut oils for the first time. In addition, we want to contribute and support the protected designation of origin (PDO) of the “Córdoba, Argentina, Peanuts” (Provincial Act N° 10.094/12). Therefore, we used the square wave voltammetry on screen-printed electrodes combined with chemometrics tools to perform these studies. At the best of our knowledge, this is the first application of screen-printed electrodes to determine Tx. In addition, we have determined and quantitated the presence of Tx in edible peanut oils for the first time using disposable devices.

PREFERRED POSITION FOR FIGURE 1

2. Materials and methods

2.1. Reagents

All reagents were of analytical grade and used as received. Ultrapure water ($\rho = 18 \text{ M}\Omega \text{ cm}^{-1}$) was obtained from a Millipore-Milli Q system. Tx was purchased from Sigma–Aldrich. Ethanol (EtOH), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), dipotassium hydrogen

phosphate (K_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4) were purchased from Merck. Tx stock solutions (6.90×10^{-4} M) were prepared in EtOH, protected from light and kept in the refrigerator. Working solutions were prepared daily by adding aliquots of the stock solution to 1 M H_2SO_4 .

2.2. *Edible peanut oil samples*

Edible peanut oil (EPO) samples were obtained from commercial markets of Río Cuarto, Córdoba, Argentina. They were stored at room temperature and protected from the light. An aliquot of 400 μ L of EPO was dissolved in 1.5 mL of EtOH / 1 M H_2SO_4 (1:4) solution and, then, was immersed in an ultrasonic bath during 30 min (brief modification with reference to our previous works) [36-38]. Then, an aliquot was taken and diluted 30 times. For the electroanalytical determinations, 75 μ L of the latest solution was placed on the SPEs.

2.3. *Instrumentation*

Voltammetric measurements were performed with an Epsilon potentiostat (BASi-Bioanalytical System, USA) using the manufacturer's electrochemical analysis software. When necessary, an external electrode Ag/AgCl, 3 M KCl (BAS, RE-5B) and a platinum wire were used as reference and counter electrodes, respectively. The SPEs connection to the electrochemical workstation was home-made. All measurements were conducted using an unmodified/bare SPE with 3-electrode configuration. A 3.1 mm diameter graphite screen-printed electrode was used as the working electrode, a carbon counter electrode and a silver ink as the pseudo-reference electrode.

2.4. *Fabrication of screen-printed electrodes*

Stencil designs with a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK) were used for SPEs production. For each SPE, a carbon-graphite ink formulation was first screen-printed onto a polyester flexible film (Autostat, 250 μ m thickness). After that, this layer was cured at 60 $^{\circ}$ C during 30 min in a box fan oven with extraction. Then, a

silver/silver chloride (60:40) reference electrode was applied by screen-printing Ag/AgCl paste (Product Code: C2040308P3; Gwent Electronic Materials Ltd, UK) onto the plastic substrate. Then, this layer was cured at 60 °C during 30 min in an oven. Finally, an insulating dielectric paste ink (Product Code: D2070423D5; Gwent Electronic Materials Ltd, UK) was printed to cover the connections and define the 3.1 mm diameter of the graphite working electrode. This layer was also cured under the same conditions as the previous layers. After these stage, the SPEs were ready to use. Potential of Ag/AgCl pseudo-reference electrode was checked by cyclic voltammetry against a commercial Ag/AgCl (3 M) electrode in the Tx / 1 M H₂SO₄ solutions. Thus, a shift of about 0.110 V to more negative values was observed for the peak potential of Tx oxidation when the pseudo-reference was used. Satisfactory stability for the pseudo-reference electrode was found and agrees very well with results recently reported [39]. These platforms have been well characterized in previous works [40].

2.5. *Square wave voltammetry measurements*

Prior to each measurement, the SPEs surface was stabilized. This stage involved to record cyclic voltammograms from -0.5 to 1.0 V (vs. Ag/AgCl pseudo-reference electrode) at a scan rate (v) of 0.100 V s⁻¹ in 1 M H₂SO₄ aqueous solution. The stage of Tx accumulation on the electrode surface was performed at -0.2 V during 90 min under non-stirring conditions. After that, the drop with Tx solution was removed and re-placed by a drop of blank solution to perform the next experiments.

SW voltammograms were recorded in the potential range from -0.5 V to 1.0 V. Other experimental parameters were: step potential, $\Delta E_s = 0.005$ V; frequency, $f = 40$ Hz and amplitude of the square wave, $\Delta E_{sw} = 0.025$ V. All the measurements were carried out at room temperature in non-deaerated solutions, using 75 μ L drop on the SPEs covering the three electrodes. Each individual experiment was carried out using a new SPEs.

3. Results and discussion

3.1. Electrochemical behavior of Tx using SPEs

Fig. 2 shows cyclic voltammograms recorded at SPEs for the blank solution (1 M H₂SO₄, line a), for Tx + 1 M H₂SO₄ solution after an accumulation time, (t_{acc}) of 90 min at open circuit potential (OCP) recorded in the presence of Tx (line b) and, then, in the blank solution (absence of Tx, line c). Tx exhibits a main oxidation peak centered at about 0.59 V in the Tx solution, while adsorbed Tx shows a peak centered at about 0.51 V in the blank solution. The reason of the anodic peak potential difference ($\Delta E_{p, b-c}$) is based on the different experimental conditions of both cyclic voltammograms. CVb was recorded in a solution of Tx (the electrooxidation of Tx is accomplished under adsorption-diffusion control), while CVc was recorded in a blank solution (the electrooxidation corresponds to Tx adsorbed on the electrode surface). The $\Delta E_{p, b-c} \approx 0.080$ V clearly indicates that the energetics related to the electrooxidation of adsorbed Tx is slightly “easier” than that of Tx in solution. In both cases, the complementary cathodic peak are observed when the direction of the potential sweep was reversed, showing the quasi-reversible nature of the electrode process. According to the Tx chemical structure (see Fig. 1), the catechol group can be oxidizable [23]. Previous results obtained in our laboratory showed that the catechol group has a quasi-reversible nature of the electrode process [41, 42].

PREFERRED POSITION FOR FIGURE 2

3.1.1. Effect of the scan rate

The influence of v on the Tx electrochemical responses was also studied by CV. Fig. S1a (Fig. S1 in Supplementary Material) shows cyclic voltammograms recorded at SPEs in 1M H₂SO₄ for a Tx concentration of 1.64×10^{-4} M after a $t_{acc} = 75$ min at OCP (non-optimized parameters, t_{acc} and E_{acc}). Therefore, the anodic peak current ($I_{p,a}$) for the Tx oxidation peak increases as v increases. Fig. S1b shows the corresponding $\log I_{p,a}$ vs. $\log v$ plot, where the slope was (0.73 ± 0.04) , $r = 0.9881$. These results allow inferring that the electron transfer

process undergoes an adsorption-/diffusion-controlled process, with strong adsorption component (slope values near to 0.5 are reported for a diffusion-controlled processes and, slope values near to 1 for an adsorption controlled process) [43].

3.1.2. Effect of the supporting electrolyte and pH on electrochemical responses

The influence of the supporting electrolyte and pH on the Tx electrochemical response were also studied. The current responses of Tx were compared in different supporting electrolytes such as 1 M H₂SO₄, 1 M HClO₄ and phosphate buffer solutions at different pH's. Fig. S2a (Supplementary Material) shows cyclic voltammograms recorded with the different supporting electrolytes at the same scan rate. These results show that higher peak currents were obtained in 1 M H₂SO₄ than in the other reaction media for a given Tx concentration (C_{Tx}^*). This reaction medium was also chosen for the Tx determination by other authors [25, 26].

The effect of pH on Tx responses at SPEs was also studied by CV. Fig. S2b (Supplementary Material) shows the relationship between the peak potentials ($E_{p,a}$) and pH for the Tx electrooxidation. The linear regression equation was $E_{p,a}$ (V) = (0.644 ± 0.015) - (0.057 ± 0.002) pH (r = 0.991). The value of the slope is very close to the theoretical value of -0.059 V, expected when the same number of electrons and protons are involved in the electrode process.

3.2. Optimization of the accumulation step

Taking into account that the process is mainly controlled by adsorption (results showed in Section 3.1.1.) stripping voltammetry technique coupled with SWV was used. Preliminary studies showed that the accumulation time (t_{acc}) and accumulation potential (E_{acc}) have a significant effect on the anodic peak current ($I_{p,a}$) responses. Fig. S3a (Supplementary Material) shows the effect of t_{acc} at OCP obtained for the electrochemical responses of Tx on SPEs by CV. Fig. S3b (Supplementary Material) depicts the effect of E_{acc} at $t_{acc} = 70$ min for

the $I_{p,a}$ of Tx on SPEs, the Tx peak current increase as the E_{acc} increase at a given t_{acc} . Therefore, a composite central design (CCD) 2^2 was used to optimize the experimental conditions to perform the Tx accumulation stage. The design was performed in eleven experiments and the levels for the two factors were selected based on the screening studies. Table 1 shows the levels studied for each factor and each run of experiments with the corresponding responses. All experiments were carried out at 1.00×10^{-6} M Tx + 1 M H_2SO_4 on SPEs by SWV.

PREFERRED POSITION FOR TABLE 1

Fig. 3 shows a graphical representation of the response surface. As it can be observed, a maximum is achieved at $t_{acc} = 90$ min and $E_{acc} = 0.200$ V. Potentials more positive than $E_{acc} = 0.2$ V are close to peak potential (≈ 0.41 V), so it was considered not convenient to explore values more positives than 0.2 V. On the other hand, taken into account that no maximum is achieved across the t_{acc} variable, accumulation times higher than 90 min can be checked still to achieved a maximum value. However, a compromise situation between the figures of merit and time consumption of the method was chosen. So, the optimization process was stopped at the values indicated. The ANOVA table (Table S1 in Supplementary Material) shows that the fitted model present an excellent correlation, determination coefficient, a low value of pure error and lack of fit value greater than 0.05 (not significant).

PREFERRED POSITION FOR FIGURE 3

3.3. Analytical parameters

Fig. 4a shows net SW voltammograms recorded under the optimized accumulation conditions. Fig. 4a also shows a significant cathodic shift of the net peak potential ($E_{p,n}$) as the Tx concentration increases. The reason for this shift is that the mechanism of Tx electrooxidation involves the formation of dimers [44]. According to theoretical studies carry out by Lovric et al. [45] the $E_{p,n}$ is shifted to cathodic potentials as the concentration of reactant increases, due to the concentration of the oxidation product is diminished by the dimerization process. Linear plot of $E_{p,n}$ on $\log c_{Tx}^*$ (not shown) gives a slope of -0.030 V/dec, which agrees very well with theory for a quasi-reversible electrode reaction coupled to the quasi-reversible dimerization of the product of the electrode reaction. The calibration plot recorded in 1 M H_2SO_4 after performing the Tx accumulation stage at the SPEs surface is shown in Fig. 4b. A linear relationship between net peak current ($I_{p,n}$), and c_{Tx}^* , was found in the concentration range from 0.05 to 1 μM . The calculated LOD was 0.021 μM , estimated as 3 times the standard deviation of the residuals ($S_{y/x}$)/slope [46].

The reproducibility of Tx determination based on SPEs was calculated as the percentage of the relative standard deviation variation of seven independent measurements of 0.25 μM Tx solution. The values obtained were 4.2 % $I_{p,n}$ and 1.1 % for the corresponding $E_{p,n}$, which are considered as very good for the devise under study.

PREFERRED POSITION FOR FIGURE 4

3.4. Interference studies

Different interfering species were explored for a possible analytical application of this electrochemical method. Therefore, the electrochemical response of 1 μM Tx was studied in the presence of daidzein (DZ), quercetin (Q), trans-resveratrol (t-Res) and caffeic acid (CA) at two concentration levels (1 and 10 μM). DZ produced a decrease in the Tx electrochemical signal near to 50 % when the concentrations ratio is 10 to 1. The decrease in Dz current signal is explained as follow. Dz has two phenolic groups (ring A and B, see Fig. S4 in Supplementary Material) that can be both oxidizable. Dz exhibits an oxidation peak centred at about 0.70 V, corresponding to the phenol oxidation of ring B (Fig. S5). According to previous reports found in the literature, the adsorption of DZ and/or its oxidation products is very strong in acid electrolytes due the phenol groups [47]. In acid media phenol groups increase the DZ hydrophobicity and, thus, its adsorption on the hydrophobic electrode surface. So, when DZ concentration increases the electrode surface is gradually blocked because of a simple competition for the active sites of the electrode and the electrochemical response of Tx is decreased (Fig. S5 in Supplementary Material). However, no change in the Tx electrochemical response was observed when the ratio between the interfering and analyte concentrations was 1. The presence of Q produced an increase in the Tx signal near to 60 and 350 % when the ratio of concentrations was 1 to 1 and 10 to 1, respectively. On the other hand, t-Res caused an increase of the Tx signal near to 50 % when the ratio between the interfering and Tx concentrations was 1 to 1. Besides, when the ratio was 10 to 1 for both, t-Res and CA, a complete overlap of the Tx signal was observed. These results can be explained considering that Q has a very similar structure to Tx. Both compounds have

catechol groups (see Fig. S4 in Supplementary Material). Chemical structure of t-Res and caffeic acid (CA) are also shown in Fig. S4. The catechol groups in rings B of Tx and Q and of CA can be oxidizable at about the same potential [48-50]. Phenolic group of t-Res is also oxidizable about that potential region as well [51]. All these compounds are oxidized from the adsorbed state on the electrode surface [48-51], leading to signals which overlap to the Tx discharge signal and, thus, increasing its peak current (see Fig S5 in Supplementary Material).

3.5. *Application of the electrochemical method to analysis of edible peanut oil samples*

The proposed electrochemical method was then applied to the determination of Tx in commercial EPO samples as a quality control parameter. It was found that the Tx presence was negligible in all commercial samples analyzed. Therefore, untreated EPO samples were spiked with different amounts of Tx (see section 2.2) and analyzed in triplicate. The results obtained are shown in Table 2. Recovery percentages varied between 95 % and 105 %.

PREFERRED POSITION FOR TABLE 2

Some electrochemical methods have recently been report to determine Tx in matrices different, using modified electrodes based on carbonaceous materials [24-28]. Although the figures of merit obtained for our sensor do not exhibit an improvement respect to the other electrochemical methods (Table 3), several advantages can be clearly highlighted, such as a low reagent consumption (75 μ L per sample), no electrode cleaning stage is necessary,

possibility of decentralized analysis and the use a simple and disposable unmodified electrode for the Tx determination.

PREFERRED POSITION FOR TABLE 3

4. Conclusions

We have studied the use of unmodified screen-printed electrodes as the portable electrochemical sensing tool towards the determination of taxifolin using both the commercial reagent as well as peanut oil samples. Therefore, we have explored different electroanalytical parameters, which have been optimized to obtain the best taxifolin sensing methodology. The importance of this development is not only due to the novelty of the proposed electrochemical method to determined taxifolin, but also to the contribution of a sensitive disposable platform for a comparative evaluation of quality control methods and the designation of origin of “Cordoba, Argentina, Peanuts”.

Acknowledgements

Financial support from Agencia Nacional de Promoción Científica y Tecnológica FONCYT (PICT 2266/2014) (PICT 2112/2015), Consejo Nacional de Investigaciones Científicas y Técnicas CONICET (PIP 112-201101- 00184), Ministerio de Ciencia y Tecnología de la Provincia de Córdoba (MINCyT) (PID 050/2010), and Secretaría de Ciencia y Técnica (SECyT) (PPI 2016-2018, Res. 331/16) from Universidad Nacional de Río Cuarto (UNRC) are gratefully acknowledged. S. A. Maccio thanks to SECyT/UNRC for the scholarship awarded.

References

- [1] M. Yang, Q. Chen, F.Y.H. Kutsanedzie, X. Yang, Z. Guo, Q. Ouyang, Portable spectroscopy system determination of acid value in peanut oil based on variables selection algorithms, *Measurement* 103 (2017) 179-185.
- [2] S. Akhtar, N. Khalid, I. Ahmed, A. Shahzad, H.A.R. Suleria, Physicochemical characteristics, functional properties, and nutritional benefits of peanut oil: A Review, *Crit. Rev. Food Sci.* 54 (2014) 1562-1575.
- [3] M. E. Carrín, A. A. Carelli, Peanut oil: Compositional data, *Eur. J. Lipid. Sci. Tech.* 112 (2010) 697-707.
- [4] M. Larrauri, M.P. Zunino, J.A. Zygodlo, N.R. Grosso, V. Nepote, Chemical characterization and antioxidant properties of fractions separated from extract of peanut skin derived from different industrial processes, *Ind. Crop. and Prod.* 94 (2016) 964-971.
- [5] M. L. Francisco, A. V. A. Resurreccion, Development of a reversed-phase high performance liquid chromatography (RP-HPLC) procedure for the simultaneous determination of phenolic compounds in peanut skin extracts, *Food Chem.* 117 (2009) 356-363.
- [6] J. Wang, X. Yuan, Z. Jin, Y. Tian, H. Song, Free radical and reactive oxygen species scavenging activities of peanut skins extract, *Food Chem.* 104 (2007) 242-250.
- [7] H. Su, Y. T. Ruan, Y. Li, J. G. Chen, Z. P. Yin, Q. F. Zhang, In vitro and in vivo inhibitory activity of taxifolin on three digestive enzymes, *Int. J. Biol. Macromol.* 150 (2020) 31-37.
- [8] S. Pan, X. Zhao, N. Ji, C. Shao, B. Fu, Z. Zhang, R. Wang, Y. Qiu, M. Jin, D. Kong, Inhibitory effect of taxifolin on mast cell activation and mast cell-mediated allergic inflammatory response, *Int. Immunopharmacol.* 71 (2019) 205-214.
- [9] F. Ge, E. Tian, L. Wang, X. Li, Q. Zhu, Y. Wang, Y. Zhong, R.-S. Ge, Taxifolin suppresses rat and human testicular androgen biosynthetic enzymes, *Fitoterapia* 125 (2018) 258-265.

- [10] A. Kim, Y. J. Nam, C. S. Lee, Taxifolin reduces the cholesterol oxidation product-induced neuronal apoptosis by suppressing the Akt and NF- κ B activation-mediated cell death, *Brain Res. Bull.* 134 (2017) 63-71.
- [11] C. Sunil, B. Xu, An insight into the health-promoting effects of taxifolin (dihydroquercetin), *Phytochemistry* 166 (2019) 112066.
- [12] S. N. Wallace, D. J. Carrier, E. C. Clausen, Batch solvent extraction of flavanolignans from milk thistle (*Silybum marianum* L. Gaertner), *Phytochem. Analysis* 16 (2005) 7-16.
- [13] R. Slimestad, T. Fossen, I.M. Vågen, Onions: A source of unique dietary flavonoids, *J. Agr. Food Chem.* 55 (2007) 10067-10080.
- [14] Y. Wei, X. Chen, X. Jiang, Z. Ma, J. Xiao, Determination of taxifolin in *Polygonum orientale* and study on its antioxidant activity, *J. Food Compos. Anal.* 22 (2009) 154-157.
- [15] Q. F. Zhang, H. Y. Cheung, The content of astilbin and taxifolin in concentrated extracts of *Rhizoma Smilacis Glabrae* and turtle jelly vary significantly, *Food Chem.* 119 (2010) 907-912.
- [16] S. Casas-Grajales, P. Muriel, The liver, oxidative stress, and antioxidants, in: P. Muriel (Ed.) *Liver Pathophysiology*, Academic Press, Boston 2017, pp. 583-604.
- [17] F. Topal, M. Nar, H. Gocer, P. Kalin, U.M. Kocyigit, İ. Gülçin, S.H. Alwasel, Antioxidant activity of taxifolin: an activity–structure relationship, *J. Enzym. Inhib. Med. Ch.* 31 (2016) 674-683.
- [18] X. Wang, H. Xia, F. Xing, G. Deng, Q. Shen, S. Zeng, A highly sensitive and robust UPLC–MS with electrospray ionization method for quantitation of taxifolin in rat plasma, *J. Chromatogr. B* 877 (2009) 1778-1786.
- [19] C. J. Yang, Z. B. Wang, Y. Y. Mi, M. J. Gao, J. N. Lv, Y. H. Meng, B. Y. Yang, H. X. Kuang, UHPLC-MS/MS determination, pharmacokinetic, and bioavailability study of taxifolin in rat plasma after oral administration of its nanodispersion, *Molecules* 21 (2016) 494-494.
- [20] S. V. Geodakyan, I. V. Voskoboinikova, J. A. Kolesnik, N. A. Tjukavkina, L.I. Vasiliy, V. I. Glyzin, High-performance liquid chromatographic method for the

determination of mangiferin, likviritin and dihydroquercetin in rat plasma and urine, *J. Chromatogr. B Biomed. Appl.* 577 (1992) 371-375.

[21] O. N. Pozharitskaya, M. V. Karlina, A. N. Shikov, V. M. Kosman, M. N. Makarova, V. G. Makarov, Determination and pharmacokinetic study of taxifolin in rabbit plasma by high-performance liquid chromatography, *Phytomedicine* 16 (2009) 244-251.

[22] Q. F. Zhang, S. C. Li, W. P. Lai, H. Y. Cheung, β -Cyclodextrin facilitates simultaneous analysis of six bioactive components in *Rhizoma Smilacis Glabrae* by capillary zone electrophoresis, *Food Chem.* 113 (2009) 684-691.

[23] P. Janeiro, O. Corduneanu, A. M. Oliveira Brett, Chrysin and (\pm)-Taxifolin electrochemical oxidation mechanisms, *Electroanalysis* 17 (2005) 1059-1064.

[24] G. Ziyatdinovaa, A. Nizamova, M. Morozov, H. Budnikov, Cyclic voltammetry of natural flavonoids on MWNT-modified electrode and their determination in pharmaceuticals, *Collect. Czech. Chem. C.* 76 (2011) 1619-1633.

[25] Y. Wu, M. Lv, B. Li, J. Ge, L. Gao, A rapid, green and controllable strategy to fabricate electrodeposition of reduced graphene oxide film as sensing materials for determination of taxifolin, *Nano* 10 (2014) 1550044.

[26] F. Wang, Y. Wu, K. Lu, B. Ye, A sensitive voltammetric sensor for taxifolin based on graphene nanosheets with certain orientation modified glassy carbon electrode, *Sensor. Actuat. B-Chem.* 208 (2015) 188-194.

[27] Q. Wang, L. Wang, G. Li, B. Ye, A simple and sensitive method for determination of taxifolin on palladium nanoparticles supported poly (diallyldimethylammonium chloride) functionalized graphene modified electrode, *Talanta* 164 (2017) 323-329.

[28] X. Zhang, D. Li, C. Dong, J. Shi, Y. Sun, B. Ye, Y. Xu, Molybdenum sulfide-based electrochemical platform for high sensitive detection of taxifolin in Chinese medicine, *Anal. Chim. Acta* 1099 (2020) 85-93.

[29] D. Martín-Yerga, I. Álvarez-Martos, M. C. Blanco-López, C. S. Henry, M. T. Fernández-Abedul, Point-of-need simultaneous electrochemical detection of lead and cadmium using low-cost stencil-printed transparency electrodes, *Anal. Chim. Acta* 981 (2017) 24-33.

- [30] S. Botasini, G. Heijo, E. Méndez, Toward decentralized analysis of mercury (II) in real samples. A critical review on nanotechnology-based methodologies, *Anal. Chim. Acta* 800 (2013) 1-11.
- [31] M. Li, D.-W. Li, G. Xiu, Y.-T. Long, Applications of screen-printed electrodes in current environmental analysis, *Curr. Opin. Electrochem.* 3 (2017) 137-143.
- [32] B. Pérez-Fernández, A. Costa-García, A. de la Escosura-Muñiz, Electrochemical (bio)sensors for pesticides detection using screen-printed electrodes, *Biosensors* 10 (2020) 32-58.
- [33] A. Smart, A. Crew, R. Pemberton, G. Hughes, O. Doran, J. P. Har, Screen-printed carbon based biosensors and their applications in agri-food safety, *TRAC-Trend. Anal. Chem.* 127 (2020) 115898-115914.
- [34] J. G. Ibanez, A. Fitch, B. A. Frontana-Uribe, R. Vasquez-Medrano, Green Electrochemistry, in: G. Kreysa, K.-i. Ota, R.F. Savinell (Eds.) *Encyclopedia of Applied Electrochemistry*, Springer New York, New York, NY, 2014 pp. 964-971.
- [35] P. Yáñez-Sedeño, S. Campuzano, J. M. Pingarrón, Electrochemical (bio)sensors: promising tools for green analytical chemistry, *Curr. Opin. Green Sustain. Chem.* 19 (2019) 1-7.
- [36] S. N. Robledo, M. A. Zon, C. D. Ceballos, H. Fernández, Qualitative and quantitative electroanalysis of synthetic phenolic antioxidant mixtures in edible oils based on their acid–base properties, *Food Chem.* 127 (2011) 1361-1369.
- [37] S. N. Robledo, V. G. L. Zchetti, M. A. Zon, H. Fernández, Quantitative determination of tocopherols in edible vegetable oils using electrochemical ultra-microsensors combined with chemometric tools, *Talanta* 116 (2013) 964-971.
- [38] S. N. Robledo, A. Y. Tesio, C. D. Ceballos, M. A. Zon, H. Fernández, Electrochemical ultra-micro sensors for the determination of synthetic and natural antioxidants in edible vegetable oils, *Sensor. Actuat. B-Chem.* 192 (2014) 467-473.
- [39] N. Rohaizad, C. C. Mayorga-Martínez, F. Novotny, R. D. Webster, M. Pumera. 3 D-printed Ag/AgCl pseudo-reference electrodes. *Electrochem. Comm.*, 103 (2019) 104-108.
- [40] G. D. Pierini, C. W. Foster, S. J. Rowley-Neale, H. Fernández, C. E. Banks, A facile electrochemical intercalation and microwave assisted exfoliation methodology applied

to screen-printed electrochemical-based sensing platforms to impart improved electroanalytical outputs, *Analyst* 143 (2018) 3360-3365.

[41] E. M. Maza, M. B. Moressi, H. Fernández, M. A. Zon, Electrochemical oxidation of fisetin: Studies related to its adsorption on glassy carbon electrodes, *J. Electroanal. Chem.* 675 (2012) 11-17.

[42] A. Y. Tesio, S. N. Robledo, H. Fernández, M. A. Zon, Electrochemical oxidation of butein at glassy carbon electrodes, *Bioelectrochemistry*, 91 (2013) 62-69.

[43] A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed., J. Wiley & Sons, Inc, New York, USA, 2001.

[44] D. A. Chernikov, T. A. Shishlyannikova, A. V. Kashevskii, B. N. Bazhenov, A. V. Kuzmin, A. G. Gorshkov, A. Y. Safronov, Some peculiarities of taxifolin electrooxidation in the aqueous media: The dimers formation as a key to the mechanism understanding, *Electrochim. Acta* 271 (2018) 560-566.

[45] M. Lovric, D. Jadresko, S. Komorsky-Lovric, Theory of square-wave voltammetry of electrode reaction followed by the dimerization of product, *Electrochim. Acta* 90 (2013) 226-231.

[46] J. N. Miller, J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, Prentice Hall, 2000.

[47] I. P. G. Fernandes, S. C. B. Oliveira, M. Ghalkhani, S. Shahrokhian, A. M. Oliveira-Brett, Electrochemical Oxidation Mechanisms of the Antioxidants Daidzein and 7-Hydroxy-4-chromone, *Electroanal.* 24 (2012) 618-626.

[48] A. M. Oliveira Brett, M. E. Ghica, Electrochemical Oxidation of Quercetin, *Electroanalysis* 15 (2003) 1745-1750.

[49] R. Abdel-Hamid, M. K. Rabia, E. F. Newair, Electrochemical behaviour of antioxidants: Part 2. Electrochemical oxidation mechanism of quercetin at glassy carbon electrode modified with multi-wall carbon nanotubes, *Arabian J. Chem.*, 9 (2016) 350-356.

[50] S. N. Robledo, J. C. López, A. M. Granero, M. A. Zensich, G. M. Morales, H. Fernández, M. A. Zon, Characterization of the surface redox process of caffeic acid adsorbed at glassy carbon electrodes modified with partially reduced graphene oxide, *J. Electroanal. Chem.* 783 (2016) 258-267.

[51] O. Corduneanu, P. Janeiro, A. M. Oliveira Brett, On the Electrochemical Oxidation of Resveratrol, *Electroanalysis* 18 (2006) 757-762.

Journal Pre-proofs

Figure captions

Figure 1. Chemical structure of taxifolin.

Figure 2. Cyclic voltammograms recorded in: a) 1 M H₂SO₄ blank solution, b) Tx solution after $t_{acc} = 90$ min at OCP, and recorded in the presence of Tx, c) and then again in the blank solution. $c_{Tx}^* = 1.64 \times 10^{-4}$ M. $v = 0.100$ V s⁻¹.

Figure 3. Response surface obtained through $I_{p,n}$ from the accumulation process. Square wave parameters: $\Delta E_{SW} = 0.025$ V, $\Delta E_S = 0.005$ V, $f = 40$ Hz.

Figure 4. a) Square wave voltammograms recorded in 1 M H₂SO₄ containing Tx at several concentrations: 0.05 μ M, 2) 0.1 μ M, 3) 0.25 μ M, 4) 0.5 μ M, 5) 1 μ M). b) The corresponding calibration plot obtained from SW voltammograms of Fig. 4 a. The accumulation conditions were: $t_{acc} = 90$ min, $E_{acc} = 0.2$ V. Square wave parameters were: $\Delta E_{SW} = 0.025$ V, $\Delta E_S = 0.005$ V, $f = 40$ Hz. The calibration curve is represented by: $I_{p,n} = (0.42 \pm 0.02) + (3.31 \pm 0.11) \cdot c_{Tx}^*$, $R^2 = 0.9959$.

Table 1. Run, factors and response for the experimental design.

Run	Factors		Response ($I_{p,n}$ / μ A)
	t_{acc} / min	E_{acc} / V	
1	90	0.20	3.42
2	60	0.10	2.76
3	103	0.10	3.5
4	90	0.00	2.93

5	60	0.10	2.44
6	60	-	2.71
		0.04	
7	18	0.10	1.88
8	60	0.24	2.92
9	30	0.00	2.40
10	60	0.10	2.47
11	30	0.20	2.86

Table 2.

Recovery assays of Tx in spiked Argentinian edible peanut oil samples.

Sample	Added / μM	Recovery / μM	Recovery / %	Relative error / %
M1	0.80	0.77	96.3	-3.75
M2	0.60	0.62	103.3	3.33

Table 3. Comparison between the proposed electrochemical method and other found in the literature.

Sensor	Sample	Linear range / μM	Electrochemical technique	LO D / μM	Reference
MWC	Pharmaceutical dosage	0.5	CV	0.2	[24]
NT-GCE	Princesfeather fruit	2 - 210		6	
ERGO-GCE	Princesfeather fruit	0.0	SWASV	0.0	[25]
ERGO-GCE	Princesfeather fruit	5 - 1.5		04	
ERGO-GCE	Princesfeather fruit	0.0	SWASV	0.0	[26]
ERGO-GCE	Princesfeather fruit	1 - 1		02	

PDDA- Gr-Pd-GCE	Fructus polygoni orientalis	0.0 4 - 1	SWV	0.0 01	[27]
MoS ₂ / ANC-GCE	Fructus polygoni orientalis	0.0 01 - 1	DPV	0.0 003	[28]
SPE	Peanut oil	0.0 5 - 1	SWASV	0.0 21	This work

Authors' individual contributions

Gastón Darío Pierini: Conceptualization; Methodology; Investigation; Software; Writing - Original Draft.

Sabrina Antonella Maccio: Conceptualization; Methodology; Software.

Sebastián Noel Robledo: Conceptualization; Methodology; Investigation; Software; Writing - Original Draft.

Alejandro García-Miranda Ferrari: Data curation; Writing- Original draft preparation

Craig Edward Banks: Data curation; Writing- Original draft preparation

Héctor Fernández: Supervision; Visualization; Writing- Reviewing and Editing; founding acquisition.

María Alicia Zon: Supervision; Visualization; Writing- Reviewing and Editing; founding acquisition.

- A novel electroanalytical method was developed to determine taxifolin in peanut oil samples.
- The electrochemical techniques used were cyclic and square wave voltammetries.
- This is the first application of screen-printed electrodes to determine taxifolin by electrochemical studies.
- The proposed electrochemical detection method provides a novel, quick, low-cost, reliable and portable method for the *in-situ* quality control of oils.

Journal Pre-proofs