# Evaluation of polyphenols in wine by voltammetric techniques with screen printed carbon electrodes

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## Abstract

The electrochemical oxidation processes that occur during a voltammetric assay in wine samples lead to the formation of species that obstructs the surface and reduce their active area. This effect is critical for screen printed carbon electrodes (SPCE ) and leads to abnormal low values of the total polyphenols content of wines, ca. 72 % lower than those obtained with glassy carbon electrodes. This effect was examined using 10 red and Port wine samples. Mechanical polishing and electrochemical-based treatments for the removal of this fouling layer were tested. The best results were obtained by electrochemical activation in at a constant potential of 1.2 V during 100 s $Na_2CO_3$ saturated solution, and by polishing.

The success of some of these treatments brings an added value to SPCE, as it opens the possibility of their reuse in the wine analysis. This outcome is particularly relevant for quality control where a huge number of analysis is performed and the reduction of cost may dictates the choice of the analytical method.

Keywords: SPCE; Electrode cleaning and activation; Polyphenols; Food analysis; DPV

## 1. Introduction

Polyphenols are plant secondary metabolites that exhibit different biological activities. They are abundant in fruits and vegetables such as grapes and berries and in drinks such as coffee, tea, and wine [1]. These compounds are accountable for the sensory properties of wines and their antioxidant activity [2]. The concentration of polyphenols in wines can vary according to the grape variety, geographical origin, soil type, harvest and winemaking technique [3].

During the past 15 years, the characterization of antioxidant properties and evaluation of the total polyphenols in wine have been successfully carried out by electrochemical techniques [1,4]. The use of cyclic voltammetry (CV) was firstly demonstrated by the work of Kilmartin using glassy carbon electrodes (GCE) [5,6]. Besides CV, differential pulse voltammetry (DPV) is increasingly used for the quantification of polyphenols in complex matrices [7,8]. In voltammetric techniques the quantification is performed by the electric current associated to the oxidation of these easily oxidizable species [1]. The detection of polyphenols by voltammetric techniques is characterized by high sensitivity and selectivity as compared with the more spread spectroscopic methods [9]. Electrochemists are continuously working in new methodologies and electrode materials [10–12] in order to improve the performance parameters of the methods and make them suitable to different sample matrices [4,7,13-15].

Despite the suitability of electroanalytical techniques, the quantification of polyphenols in routine quality control of wines is still performed using UV-vis measurements, even though this method is very susceptible to interference.

The assembly of the electrochemical cell with an arrangement of three electrodes does not facilitate the implementation of voltammetric assays by non-specialized operators. The cleaning and activation of the working electrode (WE) is an additional drawback. In complex sample analysis, the WE fouling frequently takes place due to the adsorption either of reaction products [1], or of other constituents of the matrix [16,17]. Regarding the GCE, the cleaning and activation of its surface can be performed by heat pretreatment [18], laser irradiation [19] and

exposure to ozone [20] or to radio frequency plasmas [21]. Although these techniques are very effective, they are not accessible in all laboratories, thus mechanical polishing [22] are most used electrochemical cleaning [22,23].

The mass production of integrated electrodes by screen printing techniques enabled the spread of these miniaturized devices at moderate prices. Furthermore, their use is rather easy, either by immersion or by deposition of a drop of the sample solution over the set of the three electrodes [24,25]. Despite the accessibility and simplicity of operation, these devices are not yet much used in quality control applications. This fact may be justified by the nature of these devices, that are meant for single-use. For most applications, the fouling of the WE limits the use of such devices to a single measure, increasing the cost of quality control as a large number of samples is analysed each day [26].

The use of screen printed electrodes to evaluate the content of polyphenols in wines is described in literature. In most papers, authors use the screen printed carbon electrodes (SPCE) as a platform where several active nanomaterials are deposited, such as single-walled carbon nanotubes [10], metal oxide nanoparticles ($Fe_3O_4$) [11], cerium oxide nanoparticles ($CeO_2$) [12], Laccase-Tyrosinase or Laccase [27]. In these works, the use of the SPCE based sensors in manifold analysis is not referred. Furthermore, results from these SPCE based sensors were not quantitatively compared with results from GCE. This comparison could be extremely significant as result of antioxidant / polyphenol content by GCE are widely validated in complex samples of wines [28–31], propolis [32], teas [33], fruit juices [34] regarding other methods like spectroscopic (Folin-Cicalteau [28, 30,33] , ABTS [28], [30], DPPH) or chromatographic (HPLC [30,33]).

The reuse of SPCE is an important issue in order to make them more attractive for routine measurements. However, surface treatments must be tested in order to clean and activate its surface between voltammetric measurements. Literature reports several methods to activate SPCE. Some of the methods involve the exposure to UV light from an excimer laser source [35], oxygen plasma treatment [36] and treatment with the organic solvent N,N-dimethylformamide [37]. Electrochemical based pretreatments employ the polarization of the carbon WE in the oxidation range of potentials in different solutions. The use of 0.05 M PBS solutions [38], saturated $Na_2CO_3$ solutions [39,40], 0.5 M NaOH solutions [41],

0.5 M $H_2SO_4$ solutions (cyclic voltammetry) [40], or 0.1 M $H_2SO_4$ (+5 μA for 6 min) [42]. The efficiency of these treatments was demonstrated to remove constituents organic from ink [24], to increase the surface roughness [41] or even to increase the number of chemical functionalities [41], resulting in improved kinetics of heterogeneous charge transfer. However, these treatments were not tested for the removal of impurities from the SPCE surface in between voltammetric scans. In the present work, we test the efficiency of polishing and of some electrochemical-based treatments to renewal the surface of bare commercial SPCE between assays in wine sample. The efficiency of these treatments is evaluated by comparison of data obtained in successive measurements with a single SPCE. The reliability of the polyphenol content obtained using bare SPCE is accessed by comparing these results with corresponding from a GCE. These results aim to demonstrate the SPCE reuse capability and thus contribute to the spread of voltammetric techniques in routine measurements.

## 2. Reagents and methods

*Samples characterization*

All wine samples used in this work, supplied by Sogrape Vinhos S.A., were characterized regarding current quality control parameters, following the normalized methods described in "Compendium of International Methods of Analysis" [43] namely: total acidity (method OIV-MA-FAS313- 01); non-reducing extract (method OIV-MA-AS2-03B); volatile acidity and reducing sugars [44]. Pigments, polyphenols, tannins pigments and free anthocyanins were evaluated by UV-Vis spectral readings and using calibrations maintained by the AWRI through the WineCloudTM (www.thewinecloud.com.au). These parameters were evaluated at the laboratories of ADVID (*Associação para o Desenvolvimento da Viticultura Duriense*). Free sulphur dioxide and total sulphur dioxide were evaluated by potentiometric titration following a methodology adapted from Ripper method (method OIV-MA-AS323-04B) [45].

Physical-chemical characterization parameters of ten of the eleven samples used in this work were previously reported in an earlier work [8]. Data from the eleventh sample (VT6) is reported in the supplementary material Table S1 together with

results from the other wine samples (VT1; VT2; VT3; VT4; VT5; VP1; VP2; VP3; VP4).

*Solutions and samples preparation*

Gallic acid solutions (GA, *Sigma-Aldrich*) used as standard solutions were prepared using 33 mM tartaric acid solution pH 3.20 as electrolyte. Wine samples were collected from each bottle of wine. The original cork stopper was substituted by a rubber septum stopper and wine was kept under an argon atmosphere in the dark. Sample solutions were prepared from 25 mL aliquots transferred to erlenmeyers under an argon atmosphere, by dilution (1:25; 1;50; 1:100, 1:150 and 1:200) with 33 mM tartaric acid, pH 3.20. The electrolyte solution (33 mM) was prepared from tartaric acid (*Merck*), adjusting the solution pH to 3.20 using 1.0 M NaOH.

Solutions used for the treatment and activation of the SPCE were prepared as follow. Phosphate buffer solution (T1) was prepared mixing equimolar amounts of potassium monophosphate and potassium diphosphate (*Fisher Scientific*) in order to get a total concentration of 0.05 M and pH 7.4. Solutions used in treatments T2, T3, T4 and T5 were prepared from the acquired chemicals without further purification, namely: 0.5 M sodium hydroxide (*Acros Organics*); saturated sodium carbonate (*Panreac*); 0.1 and 0.5 M sulfuric acid (*Fisher Chemical*), respectively. All solutions were prepared using ultrapure water (18 MΩ $cm^{-1}$) from Millipore Milli-Q system.

*Voltammetric assays*

Electrochemical measurements were performed at room temperature (25 ± 2 °C) using a potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by GPES 4.9 software. Differential pulse voltammograms were obtained with pulse amplitude of 100 mV, potential step of 5 mV and modulation time of 0.05 s. Two types of electrochemical cells were used: i) a conventional one-compartment cell (v=10 mL) with a GCE as working electrode (WE) (3 mm diameter; *BAS M-2012*), a platinum wire as secondary electrode (SE) and a Ag/AgCl (3 M KCl; *CH Instruments, Inc*) as reference electrode; ii) a miniaturized cell (SPCE DS 110; DropSens) composted by three screen printed electrodes (WE (2 mm diameter)

and SE made of carbon and a pseudo-reference of silver) covered by 75 µL of solution.

All potential referred across the text are quoted against the reference electrode of the corresponding electrochemical cell.

*Electrode cleaning and activation*

Before voltammetric experiments the GCE was polished on a polishing cloth with alumina suspension (0.05 µm; Tonarde 2). The electrode was thoroughly rinsed with ultrapure water and dried with an absorbent paper before recording each voltammogram.

Different treatments were carried out with SPCE to clean and activate its surface before recording each voltammogram. Results reported in Figure 1 were obtained performing 4 cyclic voltammograms (between 0 and 1 V at 100 $mVs^{-1}$) in the supporting electrolyte solution. Results in figure 2 and 3 were obtained using one of the alternative surface treatments tested. These procedures include mechanical polishing and electrochemical treatments (T1; T2; T3; T4 and T5) using different electrolyte solutions as described below.

The mechanical polishing of SPCE was performed using the same polishing materials as for GCE. A drop of alumina was deposited on a small piece (1.5 x 1 cm) of polishing cloth (Buehler) moistened with ultrapure water. This polishing tissue was gently pressured against the SPCE surface with circular movements for approximately 30 s. Then, the SPCE was rinsed abundantly with water.

Treatment T1 was carried out applying a constant potential of 2 V (vs. SPCE pseudo-reference electrode) for 100 s in a 0.05 M PBS solution pH 7.0 [38].

Treatment T2 was performed by applying a constant potential 1.4 V (vs. SPCE pseudo-reference electrode) for 30 s in 0.5 M NaOH solution [41].

Treatment T3 was carried out applying a constant potential 1.2 V (vs. SPCE pseudo-reference electrode) for 100 s in a saturated $Na_2CO_3$ solution [39,40].

Treatment T4 was based on the application of a constant current of 5 µA for 360 s in 0.1 M $H_2SO_4$ solution [42].

Treatment T5 consisted of 20 cyclic voltammetric scans from -2 V to 2 V (vs. SPCE pseudo-reference electrode), at 500 mV $s^{-1}$, in a 0.5 M $H_2SO_4$ [40].

## 3. Results and discussion

194

195 *Reuse of SPCE activated in tartaric acid solutions, pH 3.20*

196 Commercial SPCE were used to characterize the total polyphenol content (*TPP*)
197 of wines by means of voltammetric assays. Cyclic and differential pulse
198 voltammograms were recorded in diluted wine solutions (1:25) prepared from 11
199 samples of red and Port wines as described in the experimental section. These
200 results are compared with the corresponding data obtained using a GCE (Figure
201 1A**)**. Results reported in Figure 1A, expressed in equivalents of gallic acid (GA),
202 were obtained by interpolation of the integrated area under voltammograms (*IA*)
203 in calibrations curves of GA. The calibration curves of *IA* defined for GA solutions
204 using the two voltammetric techniques, CV and DPV, and the two electrodes
205 (SPCE and GCE) are presented in Table S2 (Supporting material).

206 The *IA* values obtained from DPV using the GCE are well correlated ($r$ = 0.92)
207 with the *PP* data (absorbance units) (Figure S1, supporting material). This result
208 is in accordance with our previous paper where was demonstrated using
209 chemometric tools that voltammetric results from GCE (either of CV or of DPV)
210 of red wines are well correlated with *PP* data from optical measurements [9].

211 In Figure 1A it can be observed that *TPP* values obtained from SPCE (either from
212 CV or DPV) are well correlated with those from GCE (r = 0.92). However, the
213 slope of the representation $(TPP)_{SPCE}$ *vs* $(TPP)_{GCE}$ indicates that results from
214 SPCE are about 72 % lower than those from GCE. The nature of working
215 electrodes (WE) may affect parameters such as sensitivity, selectivity or
216 analytical thresholds. Nevertheless, results from the interpolation of the
217 voltammetric signals in calibration curves should be comparable. This
218 expectation is supported by the resemblance of the voltammograms obtained by
219 the two electrode materials both in GA solutions and in wine sample solutions
220 (Supporting material, Figure S2). As the range of potentials where polyphenols
221 are oxidized is relatively far away from the solvent/ electrolyte oxidation, the
222 signals are quite clean. Besides, the DPV signals are relatively immune to the
223 contribution of the background signal that could introduce important deviations
224 when comparing results from different electrode materials. Furthermore, the
225 interferents are the same for both electrodes, even if their contribution may be
226 different in some extent.

The rather important discrepancy observed between results from the two electrodes is hardly justified by means of the previously addressed effects. Alternatively, this outcome may result from the fouling of the WE of the SPCE in the wine samples assays. In order to verify this hypothesis, a calibration curve (0.015 to 0.48 mM of GA) and a standard addition solution experiment (to a 1:25 wine sample solution) were carried out. Figure 1B exhibits data from the calibration (diamond markers) and the standard addition solution (triangle markers) experiments. These experiments were performed by DPV using a single SPCE for each experiment. Before recording each voltammogram, the SPCE was rinsed with ultra-purified water and activated by 4 voltammetric scans (0 V to 1 V, v= 100 mV $s^{-1}$) in the electrolyte solution (0.033 M tartaric acid solutions, pH 3.2). In spite of a drastic decrease of current noticed from the 1$^{st}$ to the 2$^{nd}$ and 3$^{rd}$ scans in wine samples solutions, voltammograms acquired after that were rather reproducible. The repeatability of the *IA* values of DPV voltammograms was about 8 and 12 % in GA solutions and in diluted wine samples, respectively.

Although the correlation coefficients of the two straight lines in Figure 1B are similar and adequate to these types of experiments, there is a marked difference between the slopes of the two straight lines. The slope of the calibration curve is about 5.6 times higher than that obtained for the standard addition solution. The presence of the wine markedly affected the sensitivity of the quantification of GA. In the presence of wine, the decrease of *IA* values can be assigned to the fouling of the WE surface. This effect justifies the observed discrepancy of results depicted in Figure 1A. The fouling effect lead to a substantial difference between results from calibration curve (0.59 mM (Eq GA)) and from standard addition solution methods (3.24 mM (Eq GA)).

Figure 1C exhibits values of *IA* from DPV voltammograms obtained using 5 different SPCE, each of which was used in a single diluted solution of wine (1:150, 1:100; 1:75; 1:50 and 1:25). Between scans, each SPCE surface was electrochemically activated by CV in the electrolyte (as previously described). Voltammograms recorded in the electrolyte solution, between the assays in the wine solutions, did not display any peak that could indicate the presence of adsorbed species at the electrode surface. Data obtained for the 1$^{st}$ scan from each SPCE is represented by squares, for the 2$^{nd}$ scan by triangles, for the 3$^{rd}$ scan by diamonds and for the 4$^{th}$ scan by circles markers. Data are distributed

along 3 straight-lines, which slopes decrease from the 1st to the 3rd scan. The slope decay is a result of the surface fouling, reaching a steady-state from the 3rd scan on.

In conclusion, results presented in Figure 1 clearly show that despite the relatively stability of the SPCE response obtained after the 3rd scan, the electrode fouling lead to a decrease in sensitivity. The interpolation of data from wine samples in GA calibration curves, which are not affected by this fouling effect, leads to abnormal low value of *TPP* with respect to that obtained using GCE. These results also show that the removal of this non-electroactive layer was not efficiently accomplished by the electrochemical-based treatment in the supporting electrolyte (tartaric acid).

The application of other harsher electrochemical-based treatments for removing the SPCE fouling layer formed in wine solutions are considered in the following sub-section.

*Regeneration of SPCE between successive measurements by different surface treatments*

The methods selected were the previously addressed in the introduction section, that have been developed to activate the SPCE surface by removing organic constituents of carbon inks. Although these methods were successfully increased the active surface of SPCE, their application for the removal of fouling layers was not yet tested, as far as we are aware.

These electrochemical treatments consist in the polarization of the WE in the oxidation range of potentials by potentiostatic [38,39,41], potentiodynamic [40] or galvanostatic [42] in solutions of $H_2SO_4$, NaOH, $Na_2CO_3$ or PBS.

Results in Figure 2A depict the DPV voltammograms corresponding to the 4th of a set of 6 replicates from a single SPCE and using each of treatment procedures. These procedures are described in the experimental section (T1, T2, T3, T4 and T5). For reference in Figure 2B are shown the 4th replicates of the DPV voltammograms of a SPCE and a GCE, treated by polishing between consecutive scans. The SPCE polishing was carried out using the same polishing material used for the GCE, but applying a lighter pressure on the polishing cloth, as described in the experimental section. As it can be observed, the SPCE pretreatment affects severely both the shape and the absolute value of current of

295 voltammograms of wine. For treatments T1 and T2 the peak at about 0.1 V is
296 much larger (> 16 x) than the remaining peaks. Using treatment T3 and T4, the
297 peaks high is more alike resembling more closely the profile of voltammograms
298 obtained by GCE and SPCE treated by polishing (Figure 2B). In opposition, the
299 voltammogram obtained using treatment T5 displays a quite unusual shape,
300 showing a band occurs at potentials lower than the main peak (0.1 V). These
301 results show that the electrochemical treatments can significantly modify the
302 electrode surface SPCE.
303 The oxidative conditions imposed by the electrode treatments are likely to
304 functionalize the carbon surface of the WE [38]. The different oxidative treatments
305 may have introduced different oxygen containing groups and in different extent.
306 Thus, the extent to which each electroactive molecule interact with the electrode
307 surface should dependent on the electrode pretreatment. Following this
308 reasoning, the variation of the peaks height may result from different interaction
309 degrees between molecules and/ or intermediaries of electrochemical reactions
310 with the electrode surface.
311 In Figure 2C are represented the values of *IA*, normalized by the geometric area
312 of the WE, from DPV voltammograms of diluted wine solutions obtained using
313 each treatment between assays. The effectiveness of these methods to renew
314 the electrode surface can be assessed by means of the repeatability of *IA* data
315 obtained from consecutive scans. The relative standard deviation values,
316 obtained from 6 consecutive replicates, are about 48 %, 20 %, 18 %, 23 % and
317 22 % for procedures T1, T2, T3, T4 and T5, respectively. For treatments T1 and
318 T5 *IA* values decrease continuously, indicating that the surface is not completely
319 renewed between scans. Though using treatment T4 *IA* values do not change
320 considerably, large differences are observed in the shape of voltammograms
321 from different scans. This result indicates that treatment T4 does not functionalize
322 the surface in a reproducible fashion. Regarding treatments T2 and T3, the
323 relative standard deviation results improve substantially if the first two
324 voltammograms are discarded (7 %; n=4 for T2 and 11 %; n=4 for T3). These
325 relative standard deviation values are comparable to the obtained for the
326 polishing treatments, either with the GCE (6 %) or with the SPCE (9 %) (Figure
327 2D).

To verify the significance of results obtained from a SPCE treated using T2, T3 (recognized as the most adequate treatments) and by polishing, DPV voltammograms were registered from diluted solutions of wine. Values of *TPP* (obtained by interpolation of *IA* values in calibration curve of GA) are represented against results from GCE (Figure 3A). The straight line represented in this plot corresponds to the equivalence between values ($y = x$). Points distributed along this line were obtained using the SPCE treated by the electrochemical treatment T3 (diamonds) and by polishing (squares), whereas those obtained using treatment T2 (triangles) are much below the line. These results demonstrate that only treatment T3 and polishing are adequate for the surface renewal of SPCE in voltammetric experiments in wine.

For the polishing treatment a further study was performed to evaluate the longevity of SPCE submitted to this treatment. The polishing is a rather erosive treatment due to the abrasion of alumina grains on the electrode surface. For this purpose, several voltammograms were recorded from the same wine solution polishing the SPCE surface between assays. Figure 3B shows how the results vary along the number of assays. The variability of *IA* values is about 5 % considering the first 15 values. From this assay a gradual decrease of *IA* values is notorious as all points are under the line that stands for the average. From 21$^{th}$ scan on *IA* values are outside the line corresponding to $\bar{x} - 2\sigma$ indicating that the SPCE should be discarded.

## Conclusion

The reuse of SPCE is a critical issue, as it requires the application of a surface treatment that ensures an adequate cleaning and activation of the WE between assays. The SPCE activation procedure in the electrolyte solution, that was suitable for the analysis of the standard solutions of GA, was not effective to unclog the SPCE surface after recording a voltammogram in diluted wine solutions. Although voltammograms showed an adequate level of repeatability/ reproducibility, the interpolation of data in calibration curves led to lower values of concentration of polyphenols. In order to remove the electrochemically formed layer responsible for decreasing the electrode active area, mechanical and oxidative treatments employing harsher conditions were tested. The best results

were obtained by the electrochemical activation conducted at a constant potential of 1.2 V during 100 s in a saturated solution of $Na_2CO_3$, and by polishing. The repeatability of data from wine solutions using these procedures is comparable (11% for the electrochemical treatment and 9% for mechanical polishing).


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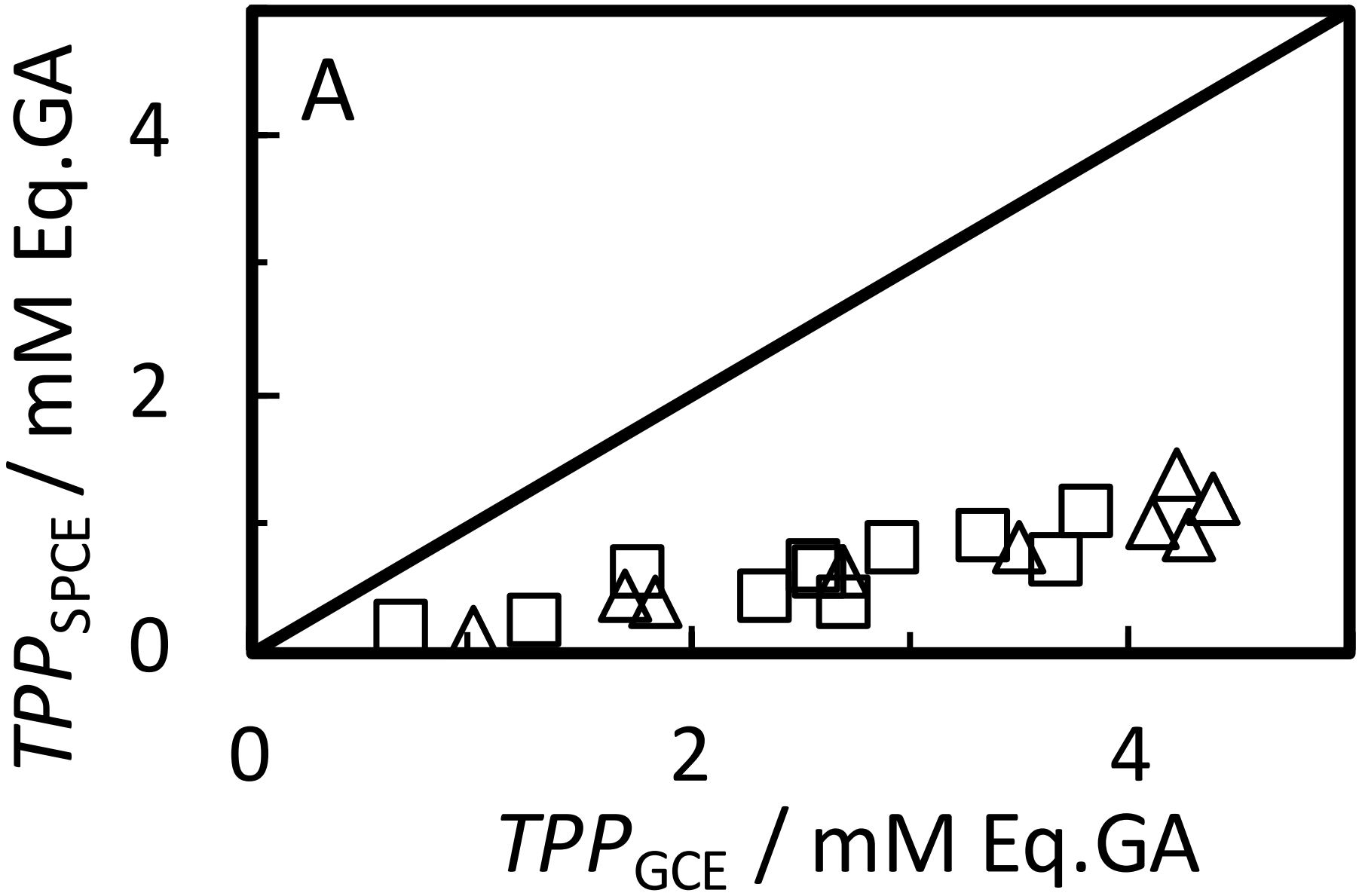
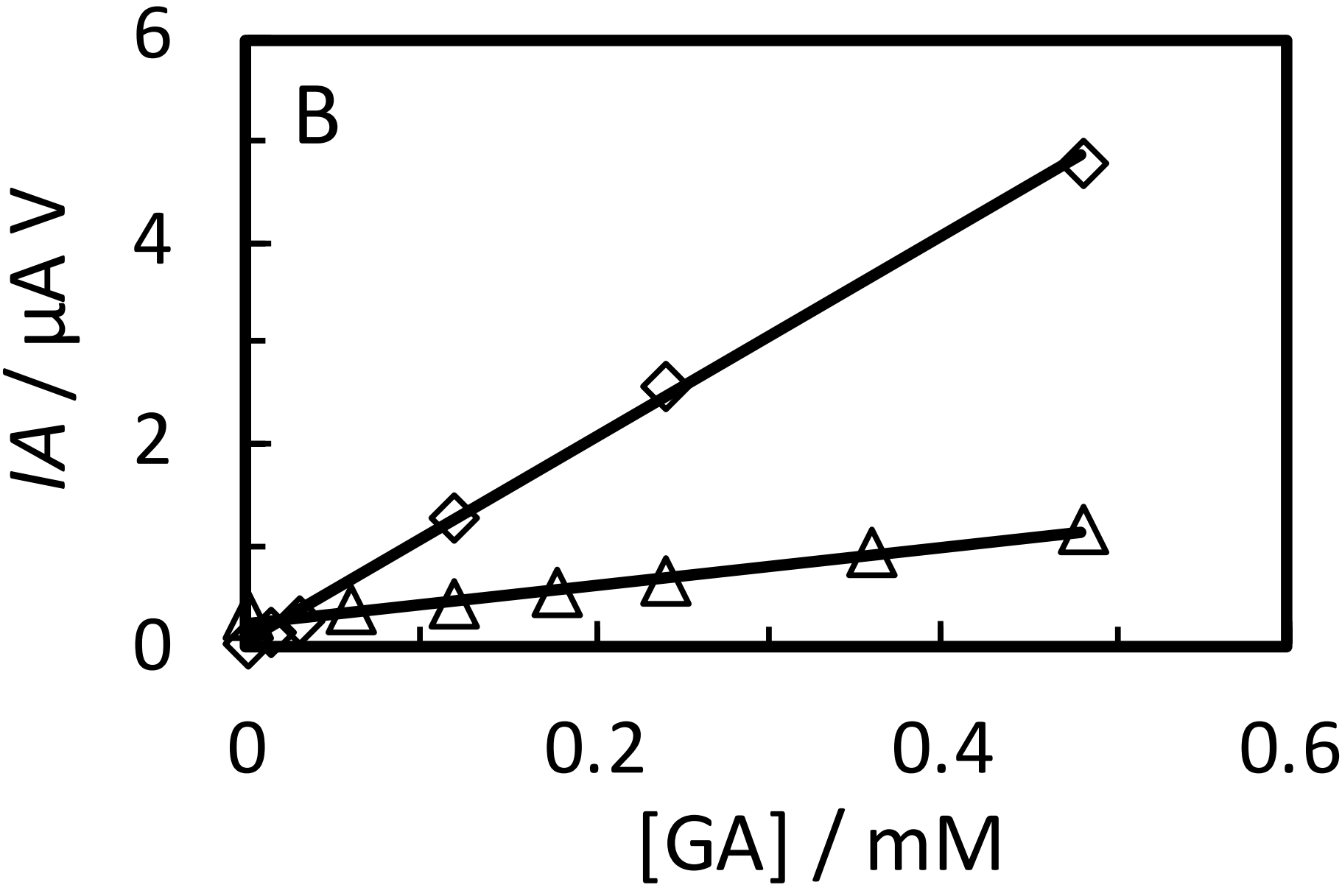
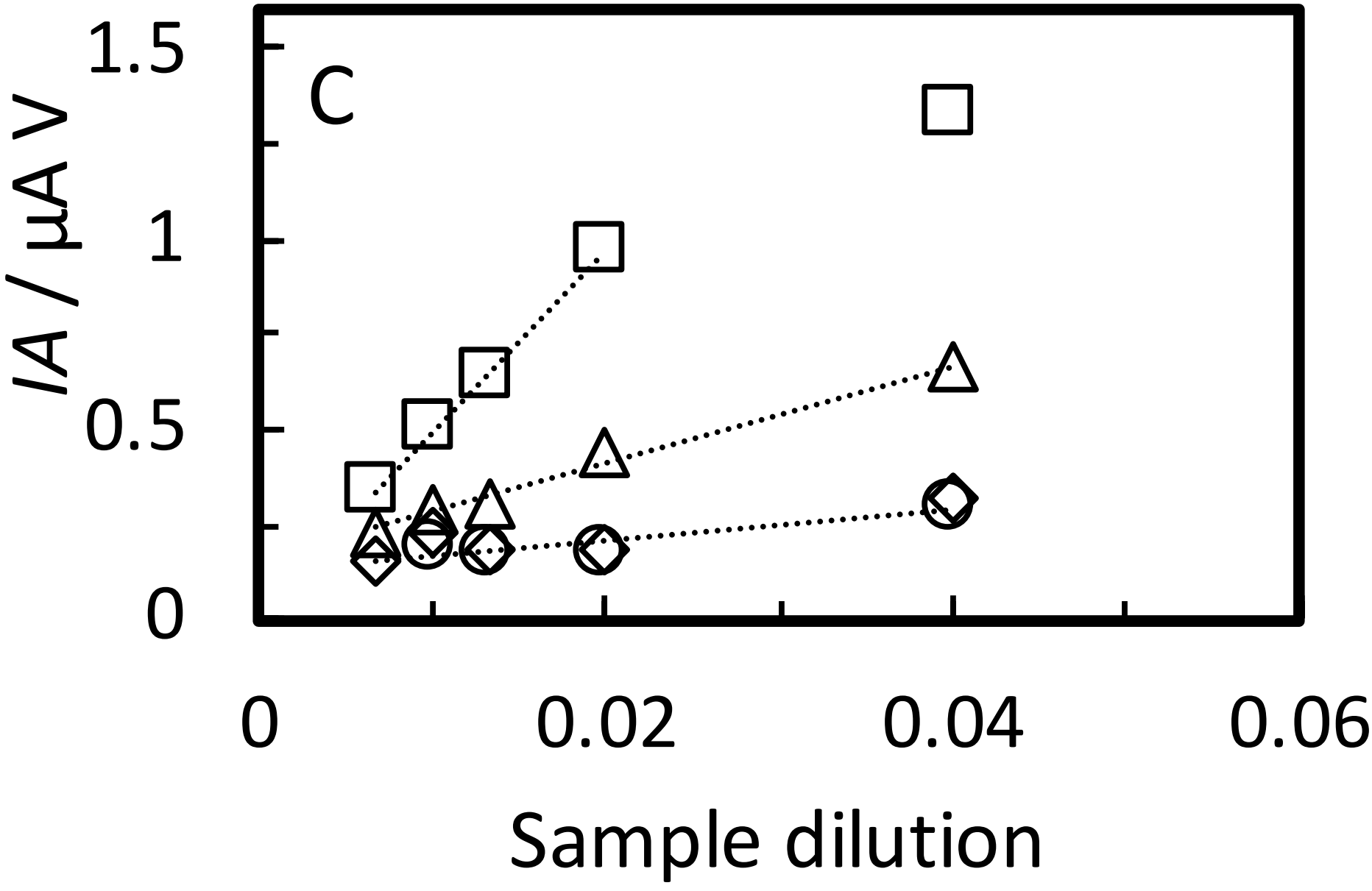
**Figure 1 – A)** Comparison of *TPP* values obtained using a SPCE and a GCE from diluted solutions (1:25) of 11 wines by CV (△) and by DPV (□); **B)** Representation of *IA* of DPV voltammograms from a SPCE corresponding to different additions of GA to an electrolyte solution (◇) and to a diluted wine solution (1:25) of VT6 (△); **C)** Variation of *IA* of DPV voltammograms of diluted wine solutions (VT6) with the number of scans (1st scan □; 2nd △; 3rd ◇ and 4th ○) using 5 SPCE (one for each diluted solution). Before each measurement, the SPCE was activated by 4 CV scans (0 to 1 V, 100 mV/s in the supporting electrolyte (tartaric acid 33 mM, pH 3.20).

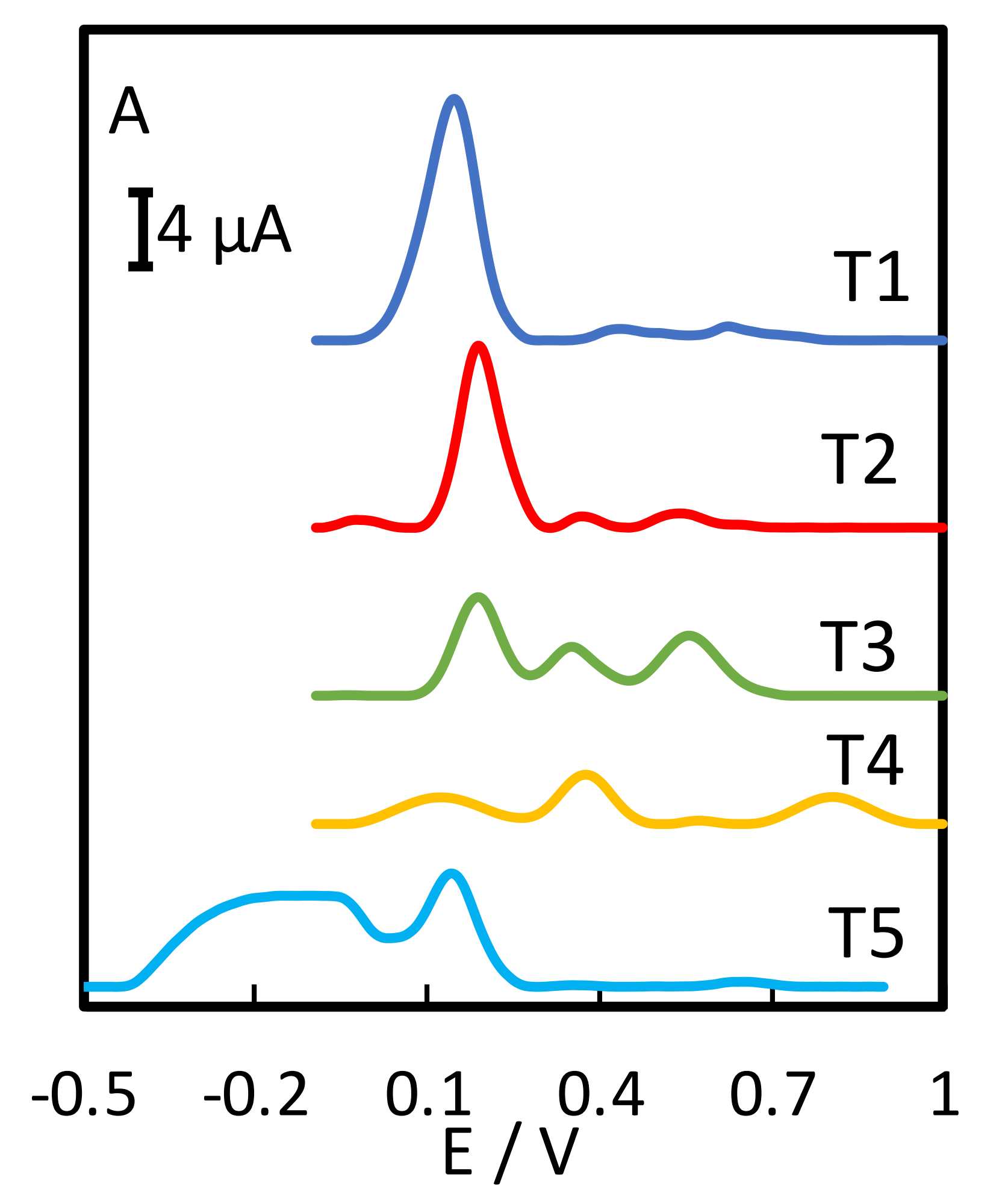
**Figure 2 –** Comparison of voltammetric results from a diluted wine solution (VT6) using SPCE activated by treatments T1, T2, T3, T4 and T5 (A and C) with those using SPCE and GCE treated by polishing (B and D). Voltammograms illustrate the 4th replicate of a series of 6 (A and B); Values of *IA* from the 6 voltammograms of: SPCE obtained for each electrochemical activation treatments (C); SPCE and GCE treated by polishing (D). Potentials are quoted with respect to the reference electrode used (Ag/AgCl for GCE and Ag pseudo-reference for SPCE)

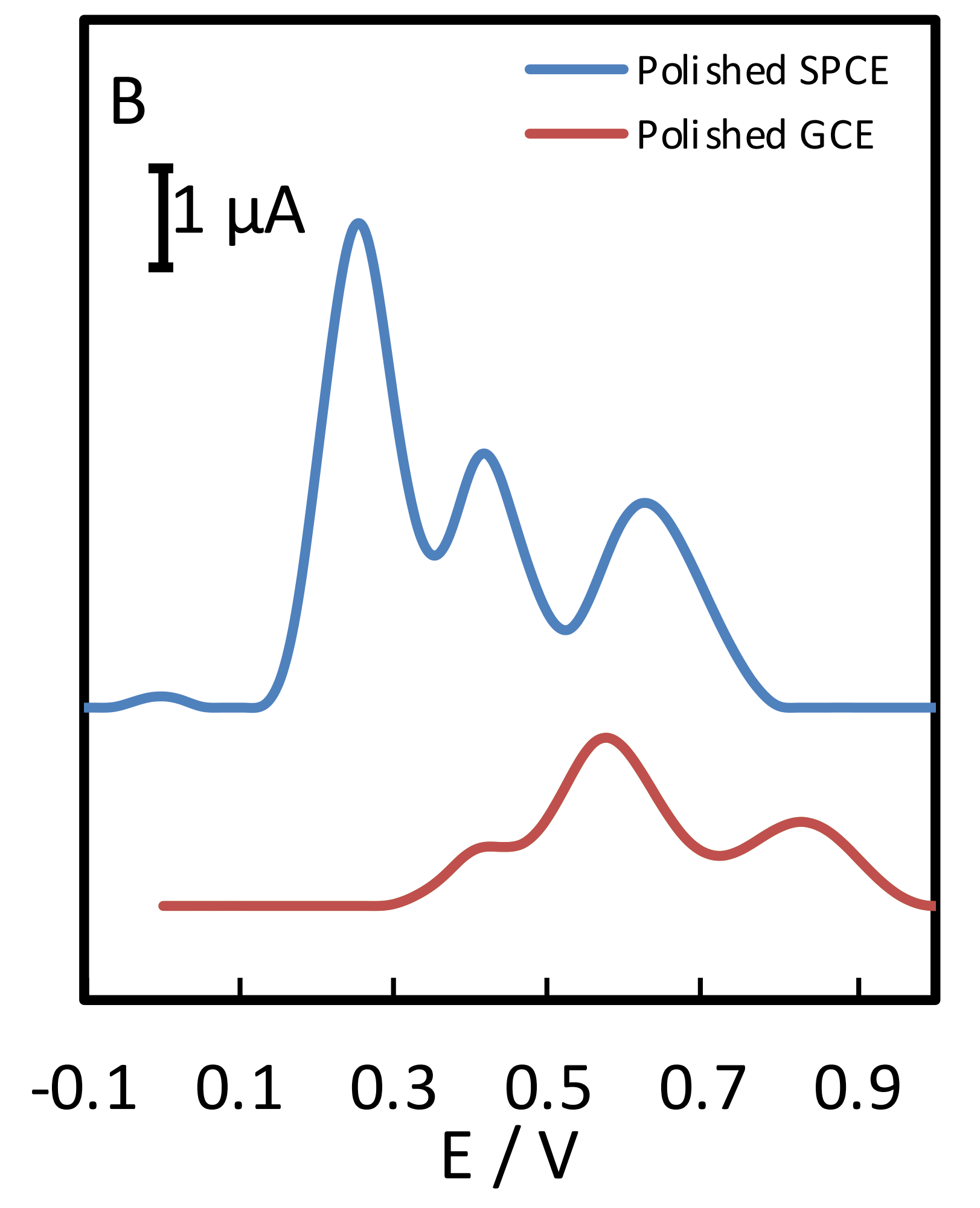
**Figure 3 A)** Comparison of *TPP* obtained using SPCE and GCE for different SPCE conditions: single-use (○); polished (□); T2 (◇) and T3 (△); **B)** Representation of *IA* values obtained from consecutive voltammograms polishing the SPCE between assays. The straight lines represent the mean, $\bar{x}$, (dashed line) and $\bar{x} \pm 2\sigma$ (solid lines) from the first 15 assays. Data was obtained by DPV from diluted solutions (1:25) of VT6.

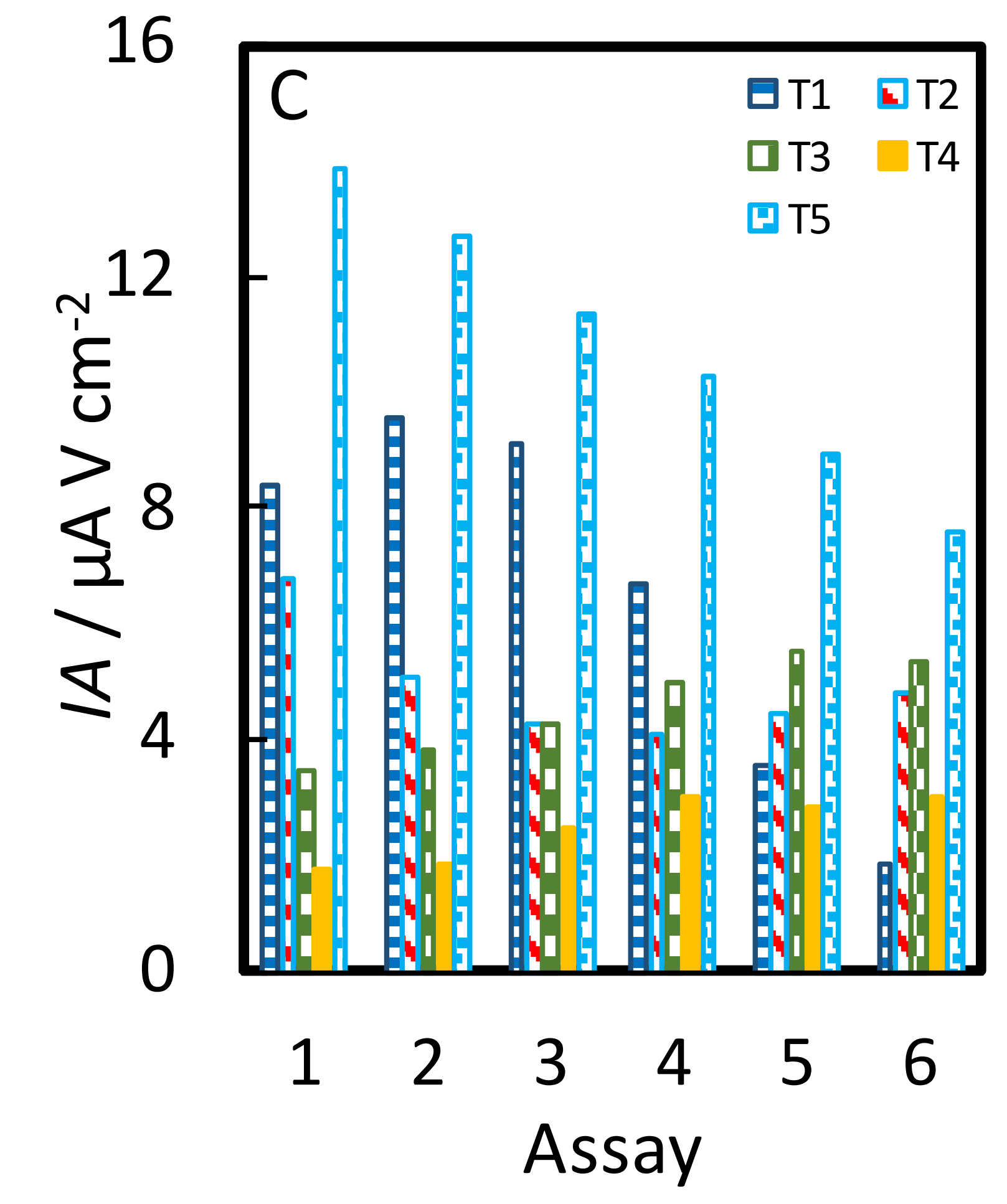

A
4
2
0
0
2
4
$TPP_{SPCE}$ / mM Eq.GA
$TPP_{GCE}$ / mM Eq.GA

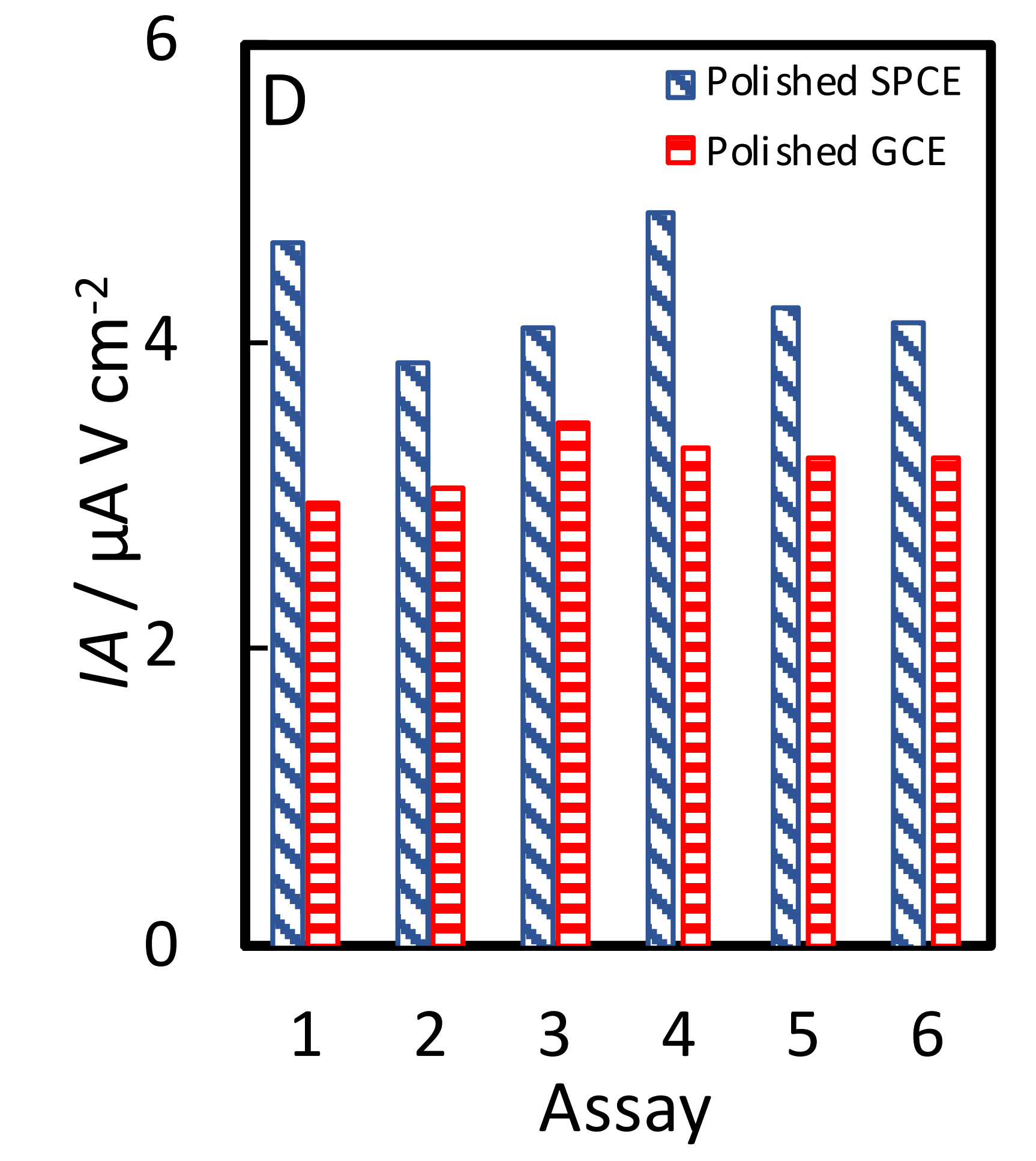

B
6
4
2
0
IA / µA V
0
0.2
0.4
0.6
[GA] / mM

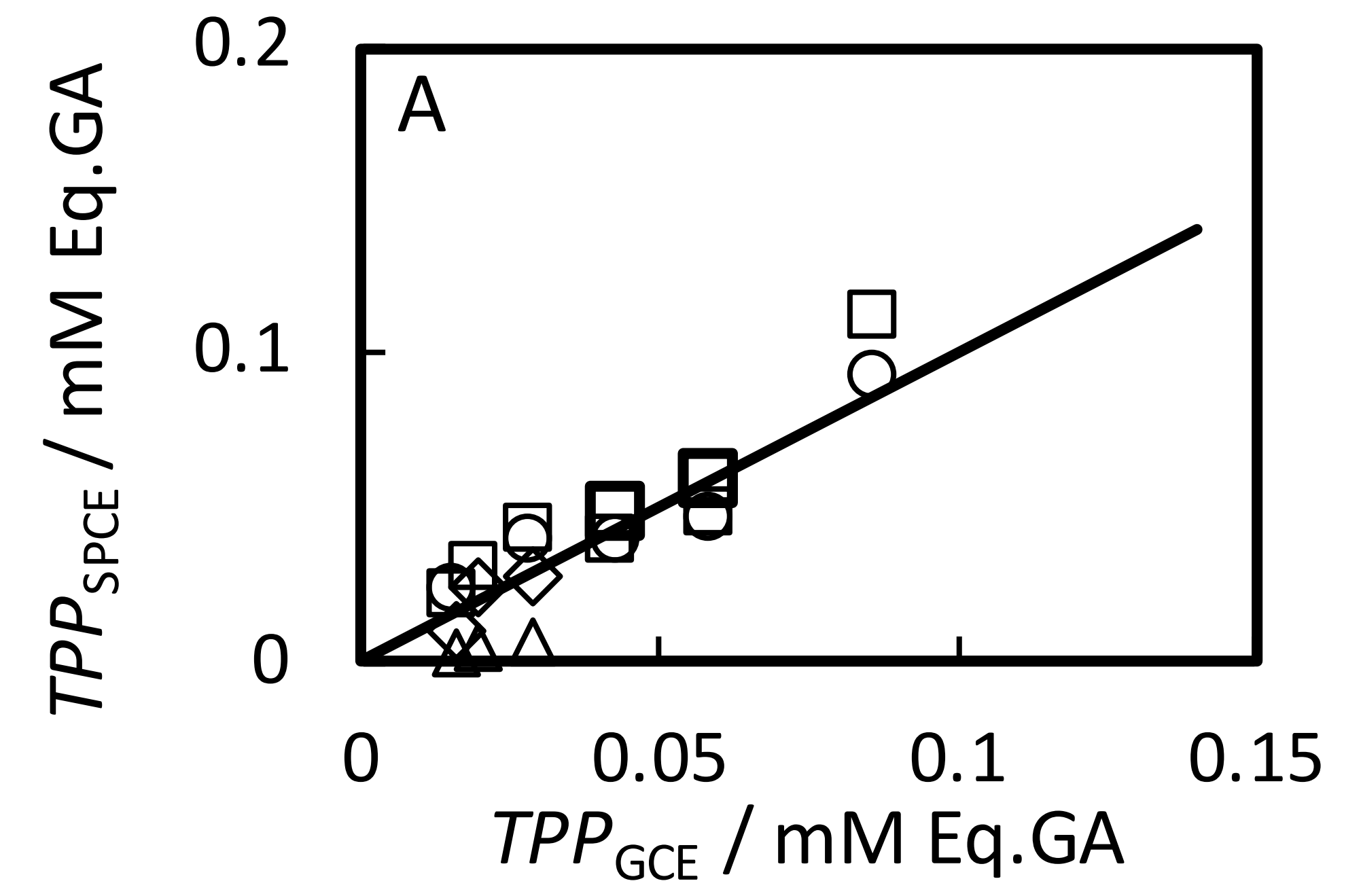

C
1.5
1
0.5
0
IA / µA V
0
0.02
0.04
0.06
Sample dilution

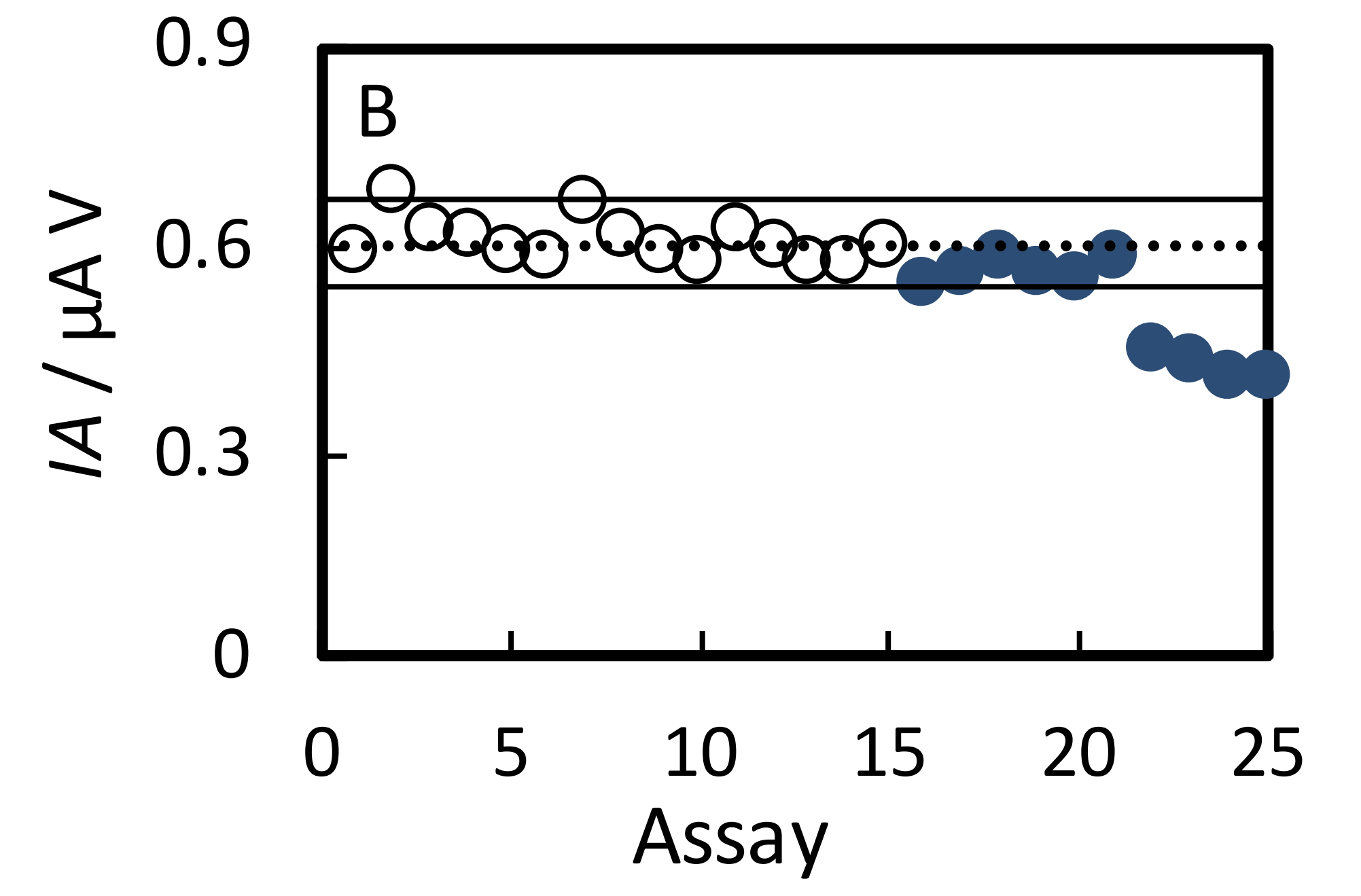

A
4 µA
T1
T2
T3
T4
T5
-0.5
-0.2
0.1
0.4
0.7
1
E / V

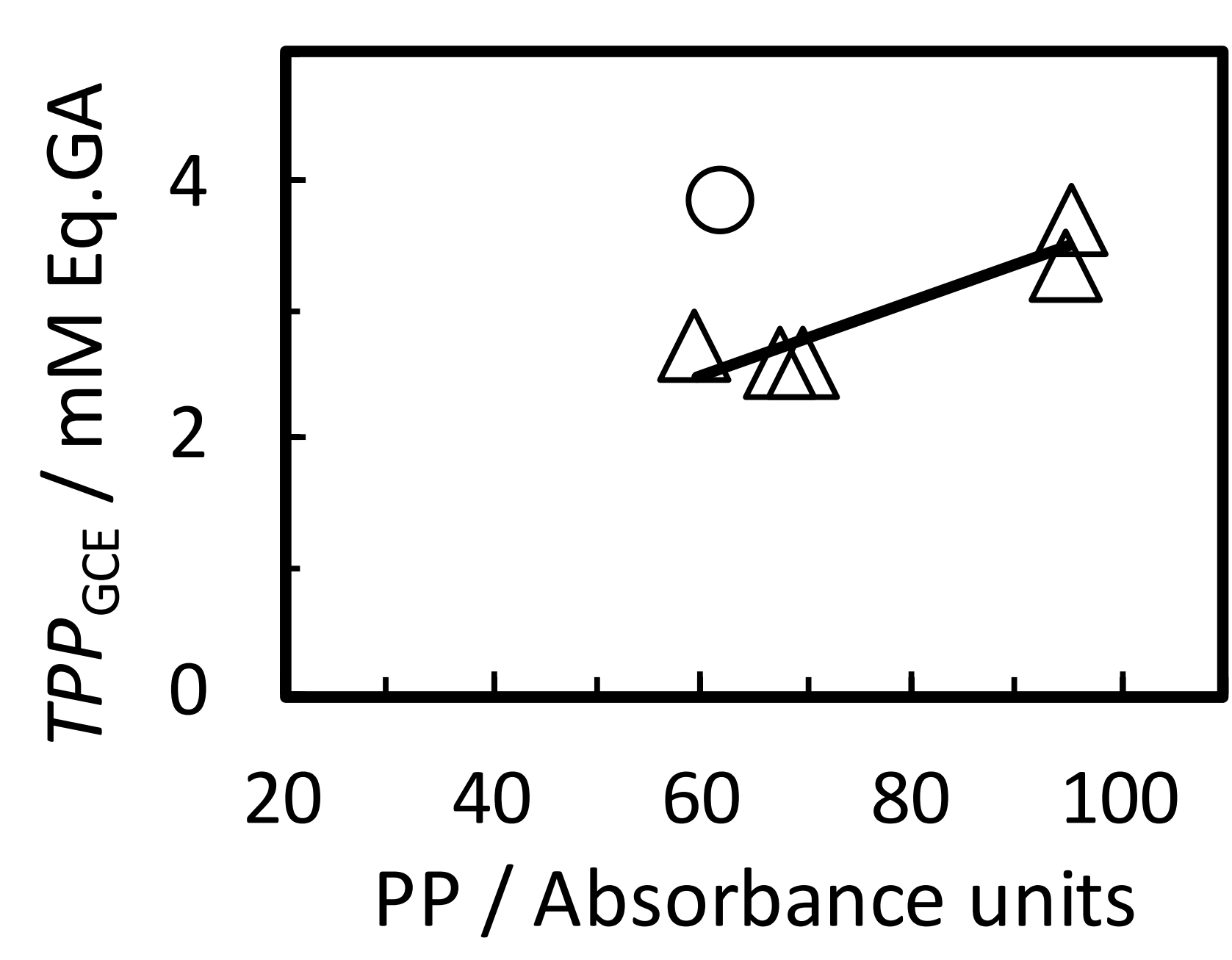

B
1 μA
Polished SPCE
Polished GCE
-0.1
0.1
0.3
0.5
0.7
0.9
E / V

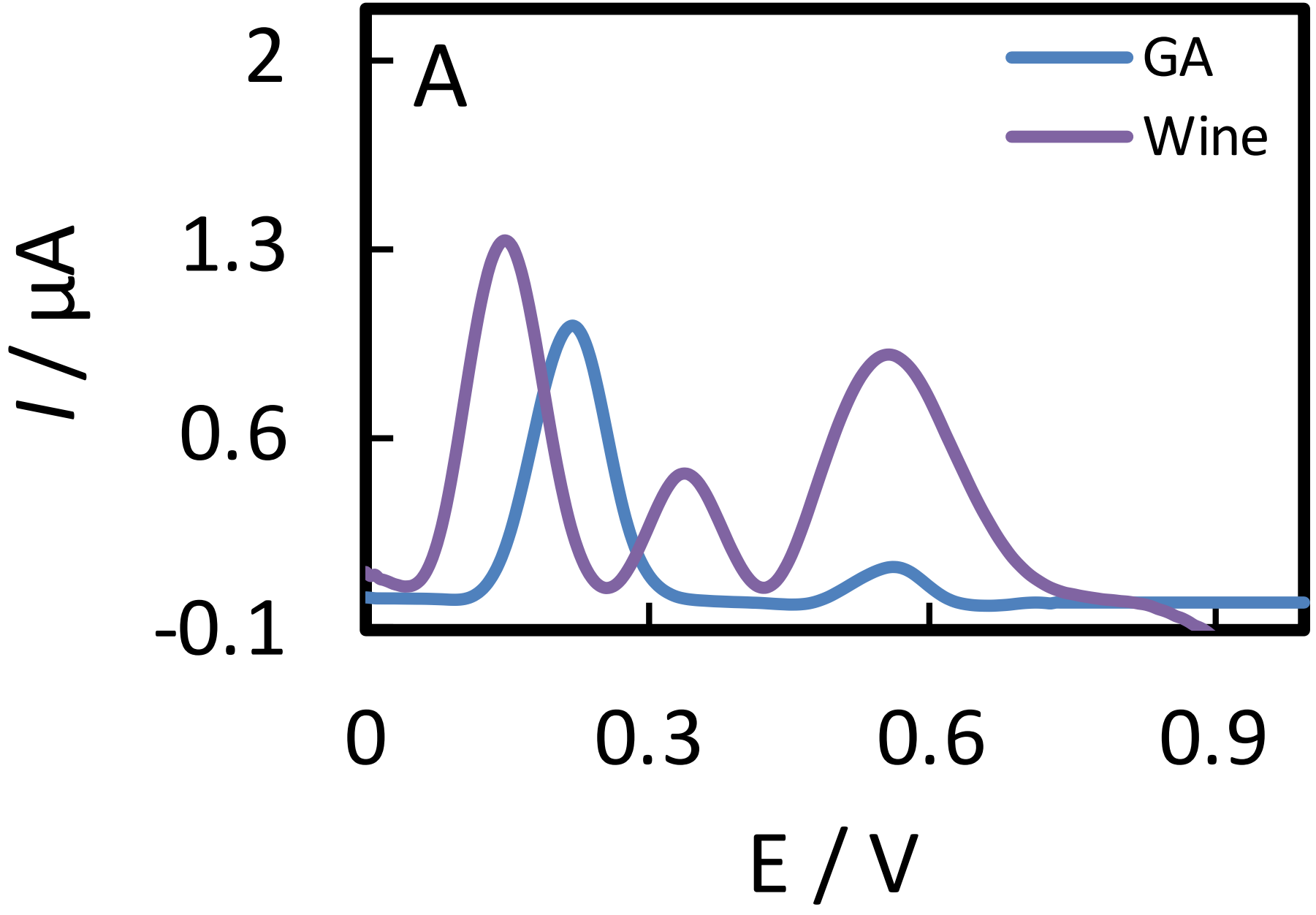

C
T1
T2
T3
T4
T5
16
12
8
4
0
IA / µA V cm-2
1
2
3
4
5
6
Assay

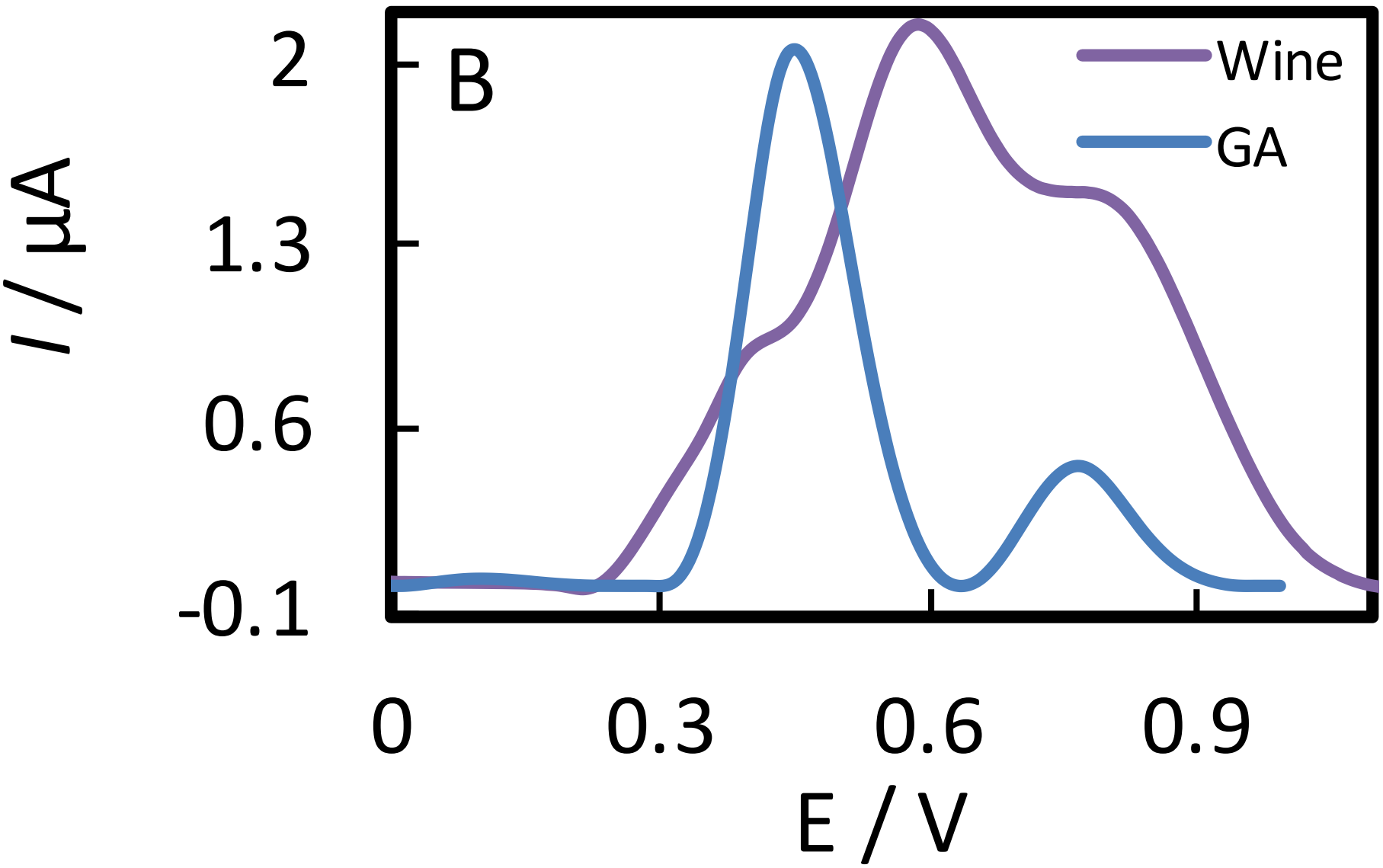

D
Polished SPCE
Polished GCE
6
4
2
0
IA / µA V cm-2
1
2
3
4
5
6
Assay


A
0.2
0.1
0
0
0.05
0.1
0.15
$TPP_{SPCE}$ / mM Eq.GA
$TPP_{GCE}$ / mM Eq.GA


B
0.9
0.6
0.3
0
IA / μA V
0
5
10
15
20
25
Assay


$TPP_{GCE}$ / mM Eq.GA
0
2
4
20
40
60
80
100
PP / Absorbance units


A
GA
Wine
2
1.3
0.6
-0.1
I / µA
0
0.3
0.6
0.9
E / V


B
Wine
GA
2
1.3
0.6
-0.1
I / µA
0
0.3
0.6
0.9
E / V