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Functionalization of Arabic Gum by Both Oxidation and Acylation: Application as Sensing Materials for the Electrochemical Determination of Phenolic Compounds

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Abstract

Novel functionalized Arabic gums (AGs) were obtained by oxidation and acylation reactions on raw Arabic gum. The synthesized materials were used as modifiers of carbon paste electrodes for the determination of quercetin (QCT), rutin (RUT) and both p-aminophenol (PAP) and acetaminophen (APAP) in 0.1 M phosphate buffer solution (PBS), pH 6.0. The identification of chemical functions on the surfaces of raw material was determined using Fourier transform infrared spectroscopy (FT-IR). Cyclic voltammetry and square wave voltammetry were used for the electrochemical study of QCT, RUT, PAP and APAP on modified electrodes. Electrochemical signals increased when the electrode was first modified with acylated gum in comparison to the unmodified electrode, and the signals became more important with the oxidized gum. Using oxidized AG modified carbon paste electrode (OAG-CPE), the linear range of the determination for both QCT and RUT was 0.020-0.090 mg/L, and from 1 to 9 mg/L for both PAP and APAP. Limits of detection were found to be 0.005, 0.023, 0.039 and 0.105 mg/L for QCT, RUT, PAP and APAP respectively. This sensor was first used for the direct quantification of APAP in commercialized tablets of Doliprane® 500 with a recovery of 94.3%, and secondly, for a simultaneous detection of both QCT and RUT in human urine.

Keywords

Acetaminophen, P-Aminophenol, Flavonoids, Oxidized Arabic Gum, Standard Additional Method, Simultaneous Determination

1. Introduction

Acetaminophen (APAP), p-aminophenol (PAP), quercetin (QCT) and rutin (RUT) are physiologically important compounds, each of them playing a vital role in several biological processes. APAP is one of the most worldwide used drugs [1]. As an antipyretic and analgesic drug, it is commonly used against mild to moderate pain. PAP is the primary hydrolytic by-product of APAP, and it is always present in pharmaceutical preparations of APAP as a synthetic intermediate or as a degradation by-product of APAP [2]. QCT and RUT are flavonoids that belong to polyphenolic compounds distributed throughout the plant kingdom and have been widely studied in drug formulations due to their specific effects on human health. APAP, PAP, QCT and RUT have been frequently detected in body fluids and pharmaceutical formulations using conventional methods including spectrophotometry [3] [4], high performance liquid chromatography [5] [6], HPLC coupled with mass spectrometry [7] [8] and electrochemistry [9]-[11]. Among them, electrochemical techniques based on modified electrodes offer some advantages such as high accuracy, fast response, good reproducibility, selectivity and the possibility of modification with cheaper materials [12] [13]. Up to now, numerous materials or compounds have been synthesized and used as modifiers for electrochemical studies of APAP, PAP, QCT and RUT. As illustration, poly (3, 4-ethylenedioxythiophene) was used as a modifier of glassy carbon electrode for a simultaneous determination of APAP and PAP [14]. Shi *et al.* [15] proposed the modification of a glassy carbon electrode by a nanocomposite of gold nanoparticles/tetraaminophenyl porphyrin for the simultaneous determination of PAP and APAP. Anuar *et al.* [16] fabricated an electrode, chemically modified with nanocomposites of platinum and graphene for the electrochemical detection of APAP. In the same way, carbon-nanotubes were used as modifiers of a carbon paste electrode for a simultaneous detection of QCT and RUT [9]. Mehmet and Necip [17] reported a glassy carbon electrode (GCE) modified by a combination of carbon nanotubes and gold nanoparticles for the simultaneous determination of QCT and RUT. Lao *et al.* [18] investigated the electrochemical detection of QCT using nanocomposites of platinum nanoparticles/poly (hydroxymethylated-3, 4-ethylenedioxylthiophene) modified glassy carbon electrode. Our previous study showed the feasibility of increasing the electrochemical signal of PAP by modifying a carbon paste electrode (CPE) with polysaccharides from raw arabic gum (AG) [13]. The results showed that the presence of Arabic Gum in the carbon paste was essential for the 1.6-fold increase in sensitivity observed in the electrochemical determination of PAP in comparison with unmodified CPE. In the similar logic, AG was pu-

rified and successfully tested as a modifier of the CPE for a sensitive electrochemical determination of QCT and RUT [19]. The obtained results showed that the use of purified Arabic gum as a modifier for a carbon paste electrode significantly increases the voltammetric signal of both QT and QT. In the present study, we have synthesized novel materials for the first time based on both acylation and oxidation of AG. The two novel functionalised materials were used to design two sensitive modified CPEs for the simultaneous determination of APAP and PAP, then both QCT and RUT. The applicability of the designed modified electrodes led to the quantification of APAP in commercialized tablets (Doliprane® 500) and for the detection of both QCT and RUT in human urine using the standard additional method.

2. Materials and Methods

2.1. Reagents and Solutions

QCT and RUT were purchased from Extrasynthese (Lyon, France). PAP and APAP were purchased from JEULIN and used as received. 0.2 g/L QCT and RUT, then 0.5 g/L PAP and APAP were prepared as stock solutions. Phosphate buffer (PBS, 0.1 M, pH 6.0) was used as working solution. All other aqueous solutions were prepared using distilled water.

2.2. Commercialized Tablets of Doliprane® and Human Urine Samples

For the determination of APAP in pharmaceutical formulations, a commercial tablet of Doliprane® was carefully weighed. It was then finely powdered and dissolved in 200 mL PBS. A 15 µL aliquot of this solution was then diluted to the mark with PBS in a 10 mL volumetric flask. The sample was finally spiked with known standard amounts of both PAP and APAP, and the unknown concentration of APAP in the tablet was determined using the standard addition method on OAG-CPE. Human urine was also used as a real matrix for quantitative analyses of QCT and RUT. Thus, a sample of urine (5 mL, pH 5.8) was diluted with 20 mL of PBS and enriched successively with 3, 5 and 7 mg/L of both QCT and RUT. The mixture was stirred for two minutes using a homogenizer and the solutions were then left to rest for 5 minutes. QCT and RUT extracted from spiked urine samples were determined using SWV on OAG-CPE and recovery rates were then calculated.

2.3. Arabic Gum

The Arabic Gum (AG) was collected from *Acacia senegal* trees in Ouagadougou (Burkina Faso) and was pretreated as previously described [19] [20]. The procedure for the AG acylation was adapted from the methodology reported by Olatunde *et al.* [21]. Briefly, 50 g of the raw gum powder was dissolved into 250 mL of distilled water and stirred for 20 min. The pH of the mixture was adjusted to 8.0 using 1 M NaOH. 5.1 g of acetic anhydride was added over a period of 1 h, while maintaining a pH range of 8.0 - 8.5. The reaction was allowed to proceed for

5 min after the addition of acetic anhydride. The pH was finally adjusted to 4.5 with 0.5 M HCl. The acylated AG was then precipitated from the solution using ethanol, filtered and washed with ethanol and air-dried.

In the same way, the oxidation of AG consisted of the introduction of 50 g of raw gum powder into 500 mL flask containing 250 mL of distilled water and stirred for 20 min to ensure complete dissolution. The pH of the mixture was adjusted to 9.5 with 2 M NaOH. 10 g of sodium hypochlorite (15% available chlorine) were slowly added into the solution over a period of 30 min while maintaining the pH range at 9.0 - 9.5. The reaction proceeded for 10 min after addition of NaOCl (15% available chlorine). After a few minutes, the pH of the mixture was adjusted to 7.0 with 1 M H_2SO_4 and the oxidized AG was then precipitated from the solution using ethanol, filtered and washed with ethanol and air-dried. Acylated and oxidized gums were powdered to obtain fine fractions less than 40 µm and then used without any further modifications for the preparation of modified carbon paste electrodes.

2.4. Apparatus

(SVW) Experiments were performed with a DY2300 electrochemical analyzer (Digi-IVY Instruments, USA) running with the DY2300 EN software and conducted using a three-electrode system, with the modified CPEs as working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Fourier transform infrared (FTIR) study was performed over the wavenumber range of 4000 - 400 cm^{-1} by the ART technique with a Bruker *α*-P FT-IR spectrophotometer with a resolution of 4 cm^{-1}. A sequence of 200 scans was recorded for each spectrum.

2.5. Preparation of Working Electrodes

The unmodified CPE was prepared according to previous work [13]. Briefly, the unmodified CPE was prepared by thoroughly hand mixing 30 mg of silicon oil with 70 mg of graphite powder (analytical grade, ultra F, <325 mesh, from Alfa) in a mortar. A portion of the composite mixture was packed into the cylindrical hole of a Teflon tube equipped with a copper wire, serving as an electrical contact with the rest of the circuit [19]. The surface exposed to the solution was polished on a weighing paper to give a smooth aspect before use. When not in use, CPEs were removed from the supporting electrolyte and stored at room temperature. Acylated and oxidized AGs modified carbon paste electrodes were prepared as described in [22] for the bare CPE using 65 mg of graphite powder, 30 mg of silicon oil and 5 mg of either acylated or oxidized gum powder.

3. Results and Discussion

3.1. Fourier Transformation Infrared (FT-IR) Spectroscopy

The FT-IR spectra of raw, acetylated and oxidized AG are presented in **Figure 1**.

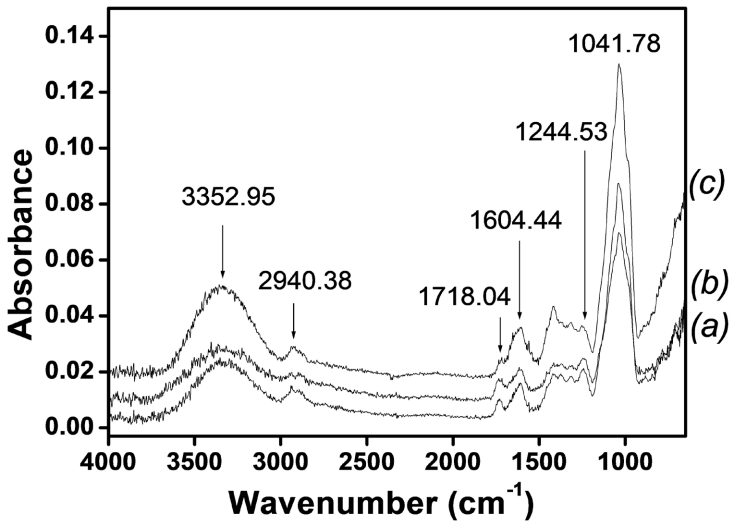

Figure 1. FT-IR spectra of (a) raw, (b) acylated and (c) oxidized arabic gum.

From **Figure 1**, the obtained spectra show a broad peak characteristic of polysaccharide units in the region 3500 - 3200 cm^{-1}, which indicates the presence of alcohols, phenols or carboxylic acids [23]. As seen, the peak at 3352 cm^{-1} increases significantly when the raw AG is oxidized (**Figure 1(c)**) and decreases when raw AG is acylated (**Figure 1(b)**). This can be explained by an increase and a decrease of OH functional groups at the surface of AG after oxidation and acylation respectively. In fact, during the acylation reaction of AG, carboxyl groups are gradually converted to $COOCH_3$ by eliminating OH functions. While AG oxidation introduces in addition to carboxyl, alcohol and phenol functions, which make the surface of the oxidized AG with OH functions [24]. The peak at 2940 cm^{-1}, indicates the presence of asymmetric and symmetric C-H stretching of aliphatic methyl and methylene. The peaks observed at 1718 cm^{-1} and 1604 cm^{-1} correspond to both carbonyl (C=O) of carboxylic acids and carboxylate, respectively. Minor peaks localized between 1500 cm^{-1} and 1244 cm^{-1} may indicate the symmetrical bending vibration of alkane bonds ($-CH_2$). The presence of C-O, C-H or C-C stretching vibrations of carboxyl groups (−COOH) is indicated by absorption peak observed at 1244 cm^{-1}. The peak at 1041 cm^{-1} is probably due to the stretching vibrations of C-O of the alcohol on the glycosyl group [18]. The obtained results from this section clearly show that new chemical functions such as alcohol, carboxylic acids or carbonyl were successfully formed at the surface of raw AG during acylation and oxidation reactions. The newly formed functions will positively interact by forming electrostatic bonds with alcohol functions of PAP, APAP and flavonoids, leading to the production of better voltammetric signals.

3.2. Electrochemical Behavior of QCT, RUT, PAP and APAP

Cyclic voltammetry was applied in 0.1 M pH 6.0 PBS containing 0.5 mg/L for each QCT and RUT and 10 mg/L for each PAP and APAP on different elaborated electrodes and **Figure 2** shows the obtained results.

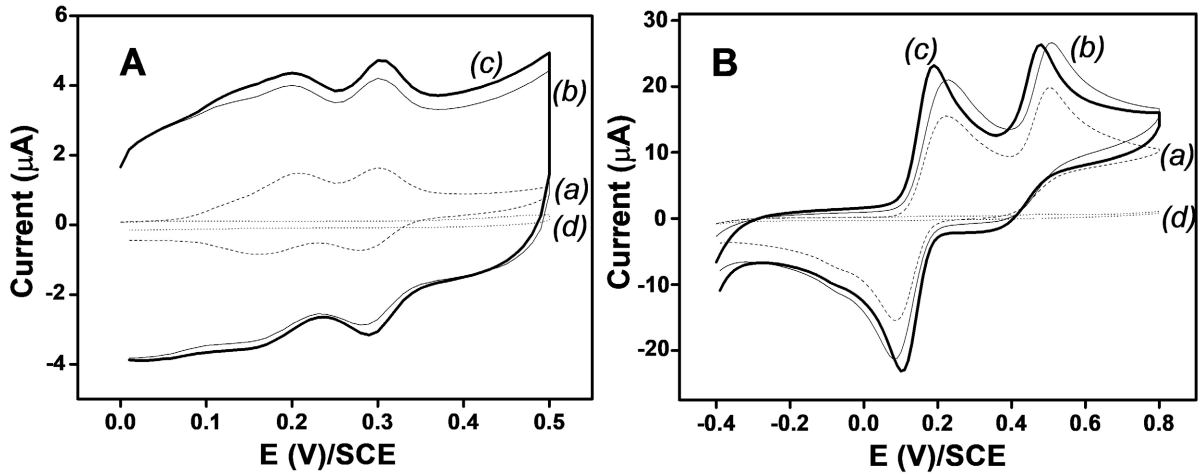

Figure 2. Cyclic voltammograms recorded on (a) bare CPE, (b) AAG-CPE and (c) OAG-CPE in 0.1 M PBS containing: (A) 0.5 mg/L for each QCT and RUT and (B) 10 mg/L for each PAP and APAP. Curve (d) corresponds to the CV behavior of OAG-CPE in blank solution. Potential scan rate: 100 mV/s.

Globally, from Figure 2, the oxidation signals of QCT, RUT, PAP and APAP obtained on both modified electrodes (AAG-CPE and OAG-CPE) are more pronounced than those on the unmodified CPE. Table 1 gives the summary of oxidation peak intensities of each analyte obtained on different tested electrodes.

Table 1. Comparison of the oxidation peak intensities of each QCT, RUT, PAP and APAP on different working electrodes.

Analytes	Peak intensities on different tested electrodes (μA)		
	CPE	AAG-CPE	OAG-CPE
QCT	4.57	5.72	5.72
RUT	5.71	10.14	10.29
PAP	12.10	12.72	16.36
APAP	10.30	12.12	12.72

From Table 1, the oxidation signal of QCT is about 4.57 μA on the unmodified CPE and increases to 5.72 μA on both acylated and oxidized modified CPE (Figure 2(a)). Similar results are observed with APAP where the oxidation signal increases from 10.30 μA to 12.12 μA and then to 12.72 μA on CPE, AAG-CPE and OAG-CPE respectively (Figure 2(b)). With RUT, a clear difference is observed between the bare CPE and the two modified electrodes with a twofold increase in the oxidation peak current (5.71 μA and 10.14 μA /10.29 μA respectively) (Figure 2(a)). The oxidation signal of PAP increases slightly from 12.10 μA to 12.12 μA on CPE and AAG-CPE respectively and becomes more pronounced (16.36 μA) on OAG-CPE (Figure 2(b)). These results can be explained by the fact that the acylation of AG introduces new functions at its surface, which interact positively with either alcohol or phenol groups of detected analytes by increasing their voltammetric signals. The OH functions increase and become more important at the surface of oxidized AG and this justifies the im-

provement of oxidation signals at OAG-CPE on the detections of QCT and RUT (Figures 2(a)-(c)), and of PAP and APAP (Figure 2(b) and Figure 2(c)). These results also demonstrate that both acylated and oxidized AG were successfully inserted into the carbon paste.

3.3. Effect of Scan Rate

Figure 3 shows cyclic voltammetric signals of 0.5 mg/L of QCT and RUT (Figure 3(a)), and of 10 mg/L of the mixture PAP and APAP (Figure 3(b)) on OAG-CPE at different scan rates.

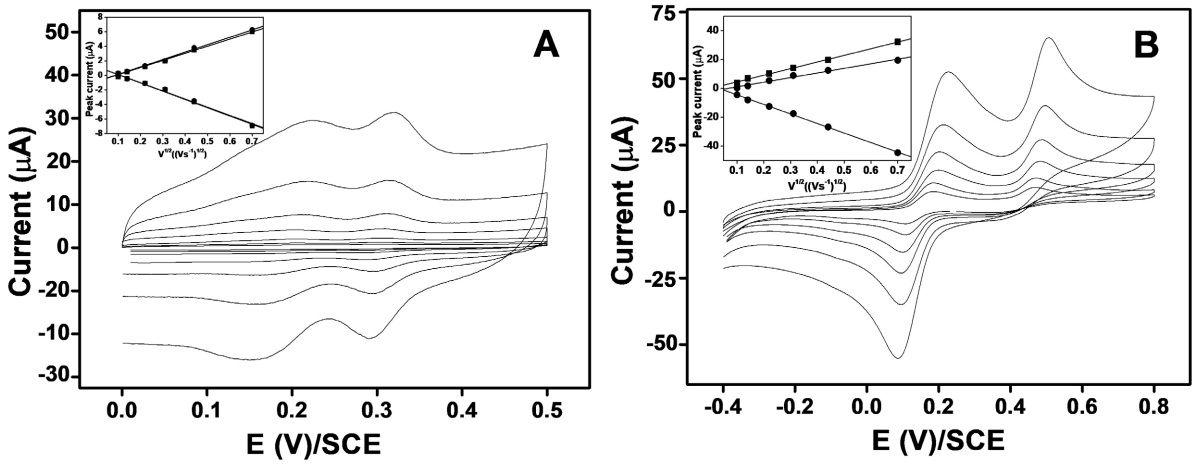

Figure 3. Cyclic voltammograms of (A) 0.5 mg/L for each QCT and RUT and of (B) 10 mg/L for each PAP and APAP in PBS at OAG-CPE with different scan rates: 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 V/s. Insets show linear dependence of Ip_a and Ip_c versus $v^{1/2}$.

Insets of Figure 3 show both oxidation and reduction peak currents of QCT, RUT, PAP and APAP on OAG-CPE, plotted against the square root of scan rates ($Ip = f(v^{1/2})$). As seen, excellent linear relationships were obtained between anodic and cathodic peak currents for both QCT and RUT (Figure 3(a)) and for both PAP and APAP (Figure 3(b)), and the square root of scan rates (v) from 0.01 to 0.5 V/s (insets of Figure 3(a) and Figure3(b)). They are expressed respectively by the following equations: $Ip_{a(QCT)}$ (μA) = $9.78\upsilon^{1/2}$ $(V/s)^{1/2}$ − 0.88 (R^2 = 0.997) and $Ip_{c(QCT)}$ (μA) = $-11.37\upsilon^{1/2}$ $(V/s)^{1/2}$ + 1.23 (R^2 = 0.993); $Ip_{a(RUT)}$ (μA) = $10.20\upsilon^{1/2}$ $(V/s)^{1/2}$ − 0.88 (R^2 = 0.995) and $Ip_{c(RUT)}$ (μA) = $-11.23\upsilon^{1/2}$ $(V/s)^{1/2}$ + 1.23 (R^2 = 0.992); $Ip_{a(PAP)}$ (μA) = $45.94\upsilon^{1/2}$ $(V/s)^{1/2}$ − 0.12 (R^2= 0.997) and $Ip_{c(PAP)}$ (μA) = $-66.13\upsilon^{1/2}$ $(V/s)^{1/2}$ + 2.07 (R^2 = 0.998); $Ip_{a(APAP)}$ (μA) = $31.92\upsilon^{1/2}$ $(V/s)^{1/2}$ − 2.12 (R^2= 0.990). These results clearly indicate that the electrode reactions correspond to a diffusion-controlled process [12] [13] [19].

In this section, CV technique was used to investigate the simultaneous and electrochemical behavior of both QCT and RUT, then PAP and APAP on different tested electrodes, and to assess the impact of acylated and oxidized Arabic gums on the carbon paste. The coming section will consist of studying the sensibility of the OAG-modified CPE towards the simultaneous quantification of both QCT

and RUT, then PAP and APAP using the SWV technique.

3.4. Calibration Curve

The analytical performance of the OAG-modified CPE for simultaneous detection of both QCT and RUT (Figure 4(a)), and of both PAP and APAP (Figure 4(b)) was studied with SWV. Figure 4 shows that the oxidation peak currents of the tested compounds increase linearly with increasing concentrations of QCT, RUT, PAP and APAP in the range from 0.02 to 0.1 mg/L for both flavonoids and from 1 to 9 mg/L for both PAP and APAP. The obtained regression equations were $Ip_{a(QCT)}$ (μA) = 1.11C (μM) − 1.21 (R^2 = 0.998); $Ip_{a(RUT)}$ (μA) = 0.22C (μM) +3.69 (R^2 = 0.982); $Ip_{a(PAP)}$ (μA) = 5.00C (μM) + 2.78 (R^2 = 0.997) and $Ip_{a(APAP)}$ (μA) = 2.69C (μM) − 2.33 (R^2 = 0.990) for QCT, RUT, PAP and APAP respectively (insets of Figure 4(a) & Figure 4(b)).

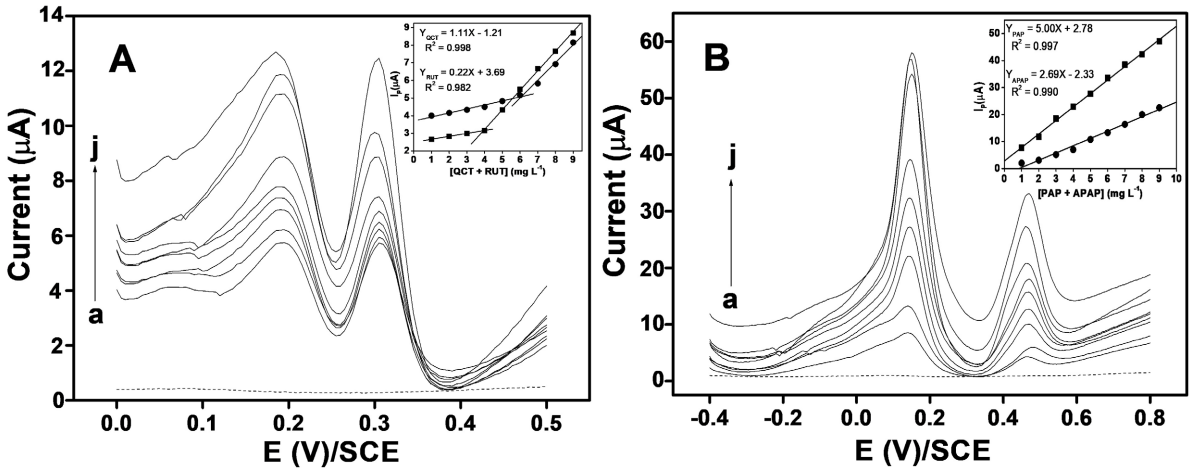

Figure 4. SWV of QCT, RUT, PAP and APAP at different concentrations in PBS on the OAG-CPE. QCT and RUT concentrations (a-j): 0, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 mg/L. PAP and APAP concentrations (a-j): 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 mg/L. Inserts show peak current versus RCT, QUT, PAP and APAP concentrations.

The limits of detection (LOD) were found to be 0.005 mg/L, 0.023 mg/L, 0.039 mg/L and 0.105 mg/L for QCT, RUT, PAP and APAP respectively, calculated using 3 S/m, where S is the standard deviation of the interception and m is the slope of the regression line [25] [26]. Table 2 gives the obtained values of standard deviation and the slope of the regression for QCT, RUT, PAP and APAP.

Table 2. Standard deviation and slope of the linear regressions for QCT, RUT, PAP and APAP.

Molecules	QCT	RUT	PAP	APAP
standard deviation	0.0018	0.0016	0.0651	0.0920
Slope (μA.L.mg^{-1})	1.11	0.22	5.00	2.69

The comparison of linear ranges and LOD of the proposed method to others previously reported in the literature is shown in Table 3.

Table 3. Comparison of the analytical performance at various electrodes in the simultaneous detection of either QCT or RUT and PAP or APAP.

Modified electrodes	pH	Linear range (mg/L)	QCT-LOD (mg/L)	QCT-LOD (mg/L)	PAP-LOD (mg/L)	APAP-LOD (mg/L)	Reference
multi-wall CNT-CPE	7.0	0.015 - 3.020 0.030 - 6.100	0.006	0.024	-	-	[17]
CPE	7.0	0.302 - 30.200 0.610 - 61.000	0.031	0.518	-	-	[27]
multi-wall CNT-GCE	7.2	0.604 - 2.416 1.220 - 4.880	0.083	0.368	-	-	[28]
PAG-CPE	6.0	0.029 - 0.329 0.060 - 0.664	0.008	0.035	-	-	[13]
[a]NDPC-CPE	6.0	0.873 - 43.656 1.208 - 60.400	-	-	0.001	0.108	[29]
[b]PEDOT-GCE	7.0	0.109 - 349.248 0.0151 - 483.200	-	-	0.130	0.060	[14]
[c]CNTs/CONH/TAPP-GCE	7.0	0.008 - 54.570 0.012 - 75.500	-	-	0.003	0.066	[15]
PAG-CPE	6.0	0.993 - 10.990	-	-	0.041	-	[19]
OAG-CPE	6.0	0.020 - 0.090 1.000 - 9.000	0.005	0.023	0.039	0.105	This work

[a]nitrogen doped porous carbon, [b]poly(3,4-ethylenedioxythiophene), [c]Gold nanoparticles/tetraaminophenylporphyrin functionalized multiwalled carbon nanotubes nanocomposites.

Globally, from Table 3, LOD of OAG-modified CPE are closer and even better in comparison to others previously reported in the literature. The principal advantage of the proposed approach is the possibility to easily and efficiently functionalize AG, in contrast to other materials used as electrode modifiers like poly (3, 4-ethylenedioxythiophene) or tetraaminophenylporphyrin [14] [15].

3.5. Application of the OAG-CPE on the Determination of APAP in Pharmaceutical Tablets

Knowing that PAP is the main by-product of APAP, the quantification of APAP in any real matrices requires to be carried out in presence of PAP. Thus, OAG-CPE was applied for the direct detection of APAP in the commercial tablets of Doliprane® 500 using the common analytical method of internal standards. Figure 5 shows SWV curves recorded on a commercial tablet of Doliprane® 500 and the insert gives the relation between peak currents and APAP concentrations.

From Figure 5, a linear relationship was obtained between the peak intensity (observed at 0.46 V versus SCE) and concentrations of added APAP. It is expressed by the following equation, $Ip_{a(APAP)}$ (μA) = 48.67C (mg/L) + 5.95 (R^2 = 0.997). The obtained results (Table 4) were in the range of the commercial limit of quality admitted by the European drugs regulation (3%) and the recovery was found to be 94.3% [12].

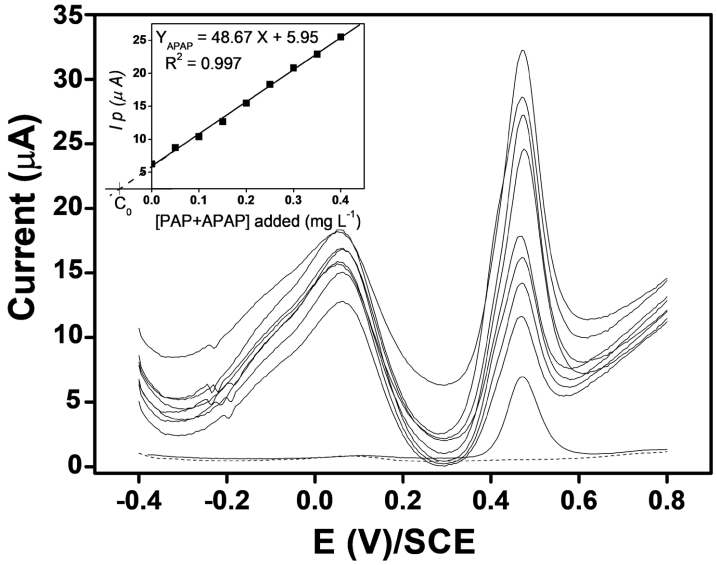

Figure 5. SWV curves recorded for the commercial tablet Doliprane 500, upon addition of known amounts of standard APAP in the supporting electrolyte. Insert displays the corresponding calibration curve.

Table 4. Determination of APAP in commercial tablets using OAG-CPE.

Doliprane® 500	Tablet initial mass (mg)	602.20 ± 1
	Tablet mass obtained after powdering (mg)	571.30 ± 1
	Theoretical APAP mass in the weighted tablet (mg)	474.09 ± 15
	APAP mass determined with OAG-CPE (mg)	447.01 ± 2
	Recovery (%)	94.30 ± 3

Secondly, OAG-CPE was used to detect QCT and RUT in human urine simultaneously. In fact, human urine samples were enriched successively with 3, 5 and 7 mg/L of both QCT and RUT and their exact amounts were determined using SWV on OAG-CPE. The results obtained are summarized in Table 5 and Figure 6 shows typical curves recorded. All the samples were determined three times under the same conditions.

Table 5. Simultaneous determination of QCT and RUT in human urine (n = 3).

Detected (mg/L)	QCT added (mg/L)	RUT added (mg/L)	QCT found (mg/L)	RUT found (mg/L)	QCT recovery (%)	RUT recovery (%)	QCT-RSD (%)	RUT-RSD (%)
-	-	-	<LOD	<LOD	-	-	-	-
-	3.00	3.00	3.67 ± 0.23	2.95 ± 0.09	122	98	7.56	2.99
-	5.00	5.00	5.67 ± 0.27	4.88 ± 0.21	113	98	5.42	4.18
-	7.00	7.00	7.45 ± 0.26	6.78 ± 0.25	106	97	3.66	3.51

From Table 4, recoveries of RUT ranged from 97% to 99%, and those of QCT ranged from 106% to 122% in human urine samples. Comparing both flavonoids,

better recovery values were obtained with RUT, showing that this method could be effective and reliable for RUT detection in urine samples as previously reported [13]. The poor determination of QCT in urine samples may be due to the presence of some interfering compounds such as urea, creatinine or uric acid, which are always present in the urine, and may interfere by increasing the voltammetric signal of QCT. This clearly indicates that such samples should be pre-filtrated before any analyses. The results also show that the present sensor, which uses oxidized AG, could be useful for the direct detection of both QCT and RUT in human urine.

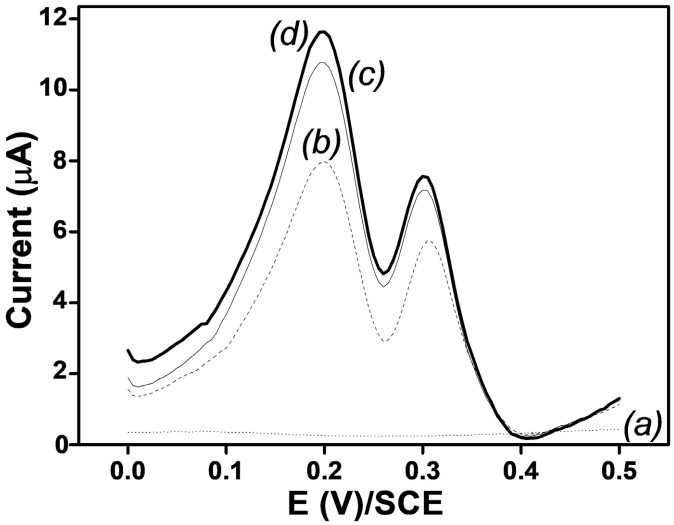

Figure 6. SWV curves recorded for QCT and RUT 3 (b); 5 (c) and 7 (d) mg/L in human urine. (a) shows the curve in the blank solution.

4. Conclusion

We demonstrated for the first time that AG can be easily and successfully functionalized by either acylation or oxidation reactions. The novel and easily functionalized AGs were successfully used as modifiers for the elaboration of two novel modified carbon paste electrodes. Both AAG-CPE and OAG-CPE significantly increase the voltammetric signals of QCT, RUT, PAP and APAP, giving rise to better and well-defined peaks in terms of sharpness and intensity on oxidized AG-CPE. As applications, the useful OAG-CPE showed to have acceptable results when used for the quantification of APAP in commercial tablets of Doliprane® 500 and then, for a simultaneous detection of QCT and RUT in human urine samples. OAG-CPE could become an alternative to the tedious, and costly modification methods by increasing the sensitivity of the analysis as well as the simplicity and low cost of electrode fabrication.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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