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Anodic Determination of Acetylsalicylic Acid at Multiwall Carbon Nanotubes-Epoxy Composite Electrode

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A novel electrochemical sensor based on a multiwall carbon nanotube within epoxy composite electrode (MWCNT-EP) has been developed for acetylsalicylic (ASA) detection. ASA is directly determined in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes without the need of a previous time-consuming alkaline hydrolysis step. ASA gives a single irreversible oxidation peak at a potential of + 0.55 V *vs.* SCE and at + 0.50 V *vs.* SCE over a wide range of concentrations, respectively.. Linear dependences of the oxidation peak current versus ASA concentrations were achieved using cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and chronoamperometry (CA). This work demonstrates that MWCNT-EP composite electrode exhibit useful properties for the direct ASA detection characterized by very good analytical parameters, *e.g.*, the sensitivity of 0.081 $mA \cdot mM^{-1}$ and the lowest limit of detection of 0.004 mM. Also, the relative standard deviation, ranged between 0.5 and 5%, demonstrates a good reproducibility of the sensor.

Keywords: multiwall carbon nanotubes-based electrochemical sensors, acetylsalicylic acid, electrochemical detection, differential-pulsed voltammetry.

1. INTRODUCTION

Acetylsalicylic acid (ASA) known as aspirin is a pharmaceutical compound of great biomedical interest due to its clinical effects on inflammation, fever, headache, and is also very efficient in

Alzheimer's disease [1,2], in prevention of cardiovascular disease [3,4], and in different types of cancer [5]. Also, acetylsalicylic acid belongs to the emerging class of pollutants in water resources, which exhibit a potential negative impact on drinking water quality and human health [6]. It is currently the subject of intensive research by chemists and fast and easy methods for its concentration determination are required.

Previous approaches, including spectrophotometry [7, 8], spectrofluorimetry [9], high-performance liquid chromatography (HPLC) [10,11], Raman spectroscopy [12, 13], and gas chromatography [14, 15] have been reported for acetylsalicylic acid determination. However, most of the above-mentioned methods are time-consuming or necessitate sample pretreatment and high cost, difficult operation, or exhibit poor performance. In contrast, it is well-known that electrochemical methods are characterized by short response time, simplicity and high sensitivity. Most recent electrodes such as the carbon paste electrode [16], the mildly oxidized boron-doped diamond electrode [17], the multi-walled carbon nanotube-alumina-coated silica nanocomposite modified glassy carbon electrode [18], and sensitive edge plane pyrolytic graphite electrode modified with graphene [19] have been reported for the sensitive determination of ASA.

Carbon nanotubes (CNTs) have been used extensively for electrochemical sensing and detection due to their special mechanical, chemical, and electrical properties. CNT-based electrochemical sensors exhibit very good electroanalytical parameters and fast response due to the useful signal enhancement provided by the electrocatalytic effect of CNTs toward the oxidation/reduction electrode process. The electrocatalytic activity depends on the synthesis method, catalyst presence, size and the defects of the CNTs [20].

In the present work, electrochemical methods for the direct determination of acetylsalicylic acid (ASA) in aqueous solution, and in a pharmaceutical drug using a multiwall carbon nanotube within epoxy composite electrode (MWCNT-EP) by cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and chronoamperometry (CA) are described. It must be mentioned that the literature data provide most information about the indirect determination of ASA by direct detection of salicylic acid (SA) as the product of ASA hydrolysis [16]. The principle of indirect determination of ASA bases on its hydrolysis on SA can be easily detected. However, there is information about the direct detection of ASA without hydrolysis at mildly oxidized boron-doped diamond electrode [17]. This study proposes an easy and fast method for direct determination of ASA in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes at a MWCNT-EP composite electrode envisaging practical application in water quality monitoring and pharmaceutical field.

2. MATERIAL AND METHODS

2.1. Materials

Commercial multiwall carbon nanotubes (MWCNTs) purchased from Nanocyl^{TM}, Belgium, were used for the composite preparation. Their main characteristics, provided by the manufacturer, are presented in Table 1. Insulating matrix consisted of two components of epoxy resin, Araldite®LY5052

and Aradur®5052 hardener, which were supplied from Huntsman Advanced Materials, Basel, Switzerland.

Table 1. Characteristics of MWCNTs given by the manufacturer

Supplier	Code	Synthesis method	CNT content (%)	Carbon purity (%)	COOH funct. (%)	Average diameter (nm)	Average length (μm)	Surface area (m^2/g)
Nanocyl™	NC7000	CCVD	90	90	-	9.5	1.5	250-300

CCVD= catalytic carbon vapor deposition process

2.2. Preparation of the MWCNT-Epoxy (MWCNT-EP) composite electrode

For the preparation of the nanocomposite, 25% wt. as-received MWCNTs have been ultrasonically dispersed into tetrahydrofuran, 99.8% (THF, Sigma-Aldrich Corporation, St. Louis, MO, USA) using a Cole-Parmer® 750-Watt Ultrasonic Processor for 10 min, followed by the homogenization with the liquid component of the epoxy resin. Subsequently, the THF was removed in vacuum at 60^o C for about 12 hours. Then, the viscous paste was homogenized on a laboratory- scale two-row mill (Collin GmbH, Germany) at 70˚C. Then, the hardener component of the epoxy resin was added and continuously mixing for 10 minutes to assure a uniform homogeneity. Finally, the resulting paste filled the cylindrical PVC tubes and cured at 80°C for 24 h. Prior to use, the electrode surface was cleaned mechanically by polishing with abrasive paper followed with 0.3 μm alumina powder (Metrohm, Switzerland) and subjected to ultrasonic cleaning for about 5 minutes in double distilled water.

Cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and chronoamperometry (CA) measurements were carried out using a computer controlled Autolab potentiostat/galvanostat PGSTAT 302 (EcoChemie, The Netherlands). The operating parameters for differential-pulsed voltammetry were step potential of 0.01 V and modulation amplitude of 0.1 V.

All measurements were conducted using a standard three-electrode cell, which consisted of a MWCNT-EP composite working electrode with 0.196 cm^2 geometrical area, a platinum wire counter electrode, and a saturated calomel as reference electrode (SCE). All experiments were carried out using a 50 mL standard cell in 0.1 M Na_2SO_4 or 0.1 M NaOH supporting electrolyte at room temperature

Three *Aspirin* tablets (OZONE, Romania) were accurately weighed and finely powdered in a mortar. An adequate amount of the powder was weighed and transferred to a 100 ml calibrated flask and dissolved in 0.3 M NaOH solution of distilled water in order to transform the target substance into a freely water-soluble salt. The supporting electrolytes used for the electrochemical experiments are 0.1 M KNO_3, 0.1 M NaOH, and 0.1 M Na_2SO_4 solutions, which were prepared in distilled water from analytical grade reagents provided by Merck.

3. RESULTS AND DISCUSSION

The MWCNT-composite exhibited a very good distribution of the multiwall carbon nanotubes within the epoxy matrix, which was shown by SEM imaging, as we reported in our previous paper [21].

3.1. Electrochemical characterization of the MWCNT-EP composite electrode using classical ferro/ferricyanide system

The ability to obtain kinetic information and detection operating parameters from voltammetry measurements requires precise determination of the oxidation/ reduction current peak positions and areas [22-25].

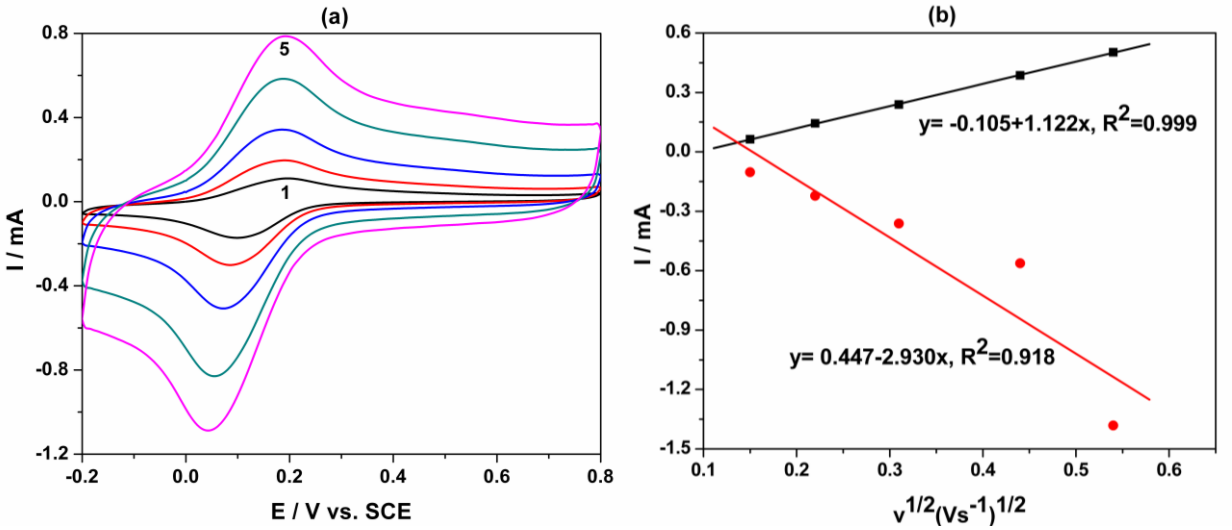

Figure 1. a. CVs of the MWCNT-EP composite electrode recorded in 4 mM $K_3[Fe(CN)_6]$ in 0.1 M KNO_3 supporting electrolyte at different scan rates: 1) 0.025, 2) 0.05, 3) 0.1, 4) 0.2, 5) 0.3 Vs^{-1}. **b.** Calibration plots of the oxidative and reductive peak currents *vs.* square root of scan rate.

Potassium ferricyanide ($K_3[Fe(CN)_6]$) is used as a probe to determine the electroactive surface area of the MWCNT-EP composite electrode. Cyclic voltammetry (CV) of 4 mM $K_3[Fe(CN)_6]$ in 0.1 M KNO_3 supporting electrolyte at the MWCNT-EP composite electrode was recorded at different scan rates (Fig. 1a).

According to the Randles–Sevcik equation (1)

$$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} v^{1/2} C \quad (1)$$

where A represents the area of the electrode (cm^2), n the number of electrons participating in the reaction (and is equal to 1), D the diffusion coefficient of the molecule in solution, C the concentration of the probe molecule in the solution and is 4 mM, and v is the scan rate (Vs^{-1}), the linear dependence between peak current and the square root of the scan rate is represented in Fig. 1b. Based on the slope, the apparent diffusion coefficient of $K_3[Fe(CN)_6]$ was determined to be 5.33×10^{-6}

cm^2s^{-1}. By comparison with the theoretical diffusion coefficient value of 6.7×10^{-6} cm^2s^{-1} found in the literature [25], the value of the electroactive surface electrode area was determined to be 0.173 cm^2 *vs.* the value of the electrode geometric area of 0.196 cm^2, which is direct related to the multiwall carbon nanotubes distribution within epoxy matrix.

3.2. Cyclic voltammetry measurements

The electrochemical behavior of ASA on the MWCNT-EP composite electrode was examined by cyclic voltammetry (CV) measurements using 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes. Fig. 2a presents the series of the CVs recorded at the MWCNT-EP composite electrode in 0.1 M Na_2SO_4 supporting electrolyte with ASA concentrations ranging from 0.02 mM to 1.2 mM. For this ASA concentration range, a linear dependence of the oxidation peak currents recorded at +0.55 V/SCE *vs.* ASA concentrations was found, and a very good sensitivity (0.063 $mA \cdot mM^{-1}$) was obtained.

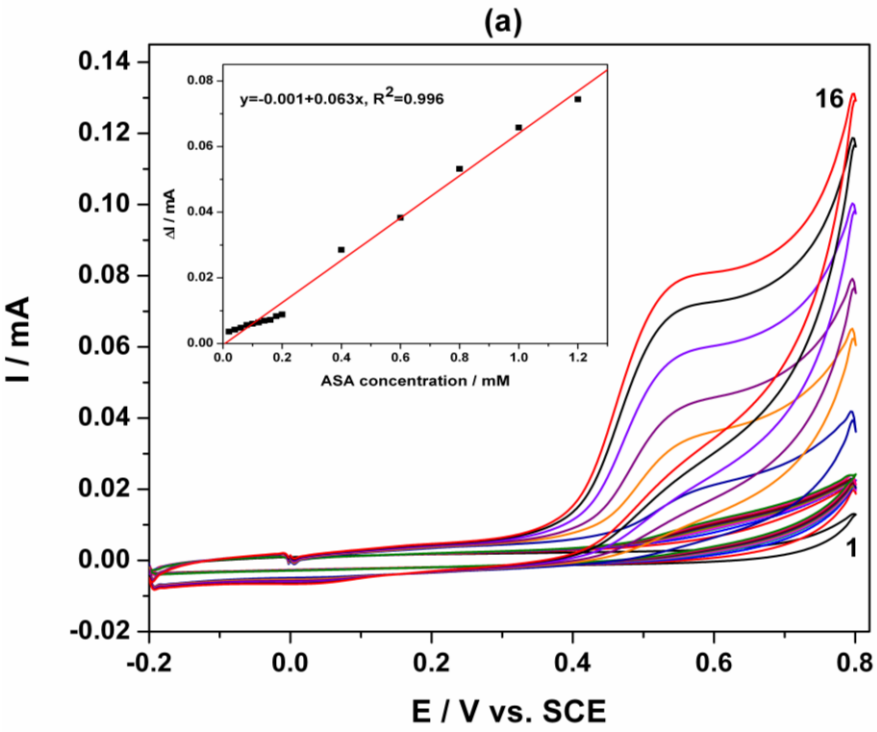

Figure 2a. CVs of the MWCNT-EP composite electrode recorded in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of: 2) 0.02; 3) 0.04; 4) 0.06; 5) 0.08; 6) 0.1; 7) 0.12; 8) 0.14; 9) 0.16; 10) 0.18; 11) 0.2; 12) 0.4; 13) 0.6; 14) 0.8; 15) 1; 16) 1.2 mM ASA; scan rate of 0.05 Vs^{-1}. Inset: the calibration plots of the anodic currents recorded at E= + 0.55 V/SCE vs. ASA concentration.

Similar detection experiments for ASA determination were performed using a 0.1 M NaOH supporting electrolyte and the results are presented in Fig. 2b. The calibration plots of the anodic peak currents *vs.* ASA concentrations exhibited good linearity and similar sensitivity as in the case of Na_2SO_4- supporting electrolyte range (see Table 2).

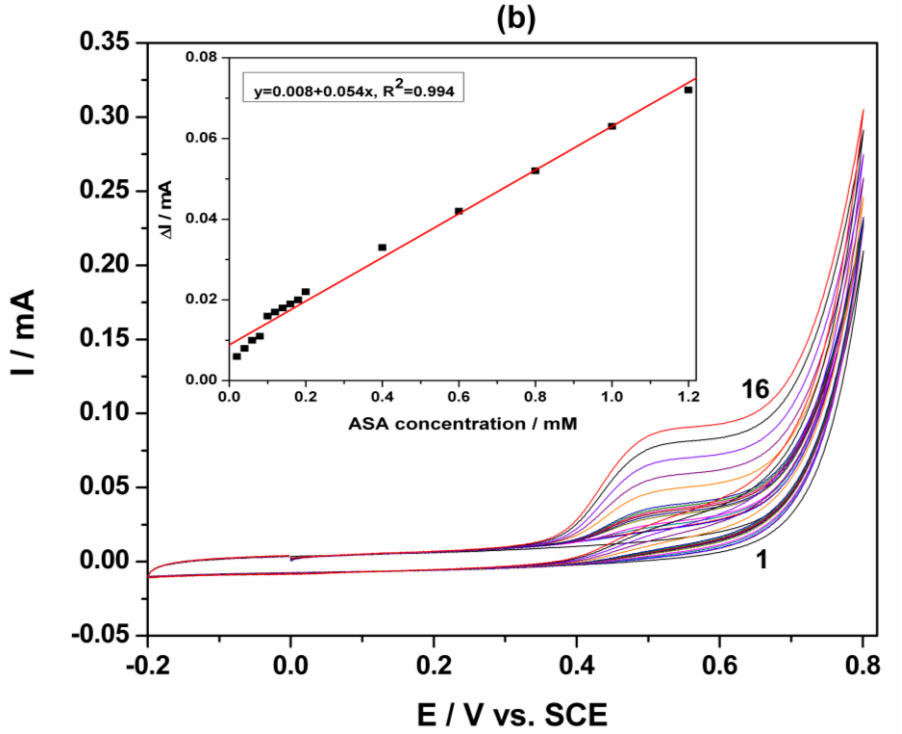

Figure 2b. CVs of the MWCNT-EP composite electrode in 0.1 M NaOH supporting electrolyte (curve 1) and in the presence of: 2) 0.02; 3) 0.04; 4) 0.06; 5) 0.08; 6) 0.1; 7) 0.12; 8) 0.14; 9) 0.16; 10) 0.18; 11) 0.2; 12) 0.4; 13) 0.6; 14) 0.8; 15) 1; 16) 1.2 mM ASA; scan rate of 0.05 Vs^{-1}. Inset: the calibration plots of the anodic currents recorded at E= +0.50 V/SCE vs. ASA concentration.

In contrast with literature data related to the lack of a direct oxidation peak on a carbon paste electrode, reported by Supalkova [16], our results reveal that MWCNT-EP composite electrode exhibits electrocatalytic activity towards the direct ASA oxidation at the potential value of +0.55 V and +0.50 V/SCE, respectively. Also, this electrode exhibited superiority compared to a boron-doped diamond electrode [16] with regard to sensitivity and the detection potential value, a less positive detection potential is desired to minimize the interference potential.

The effect of the scan rates in the range from 0.01 Vs^{-1} to 0.5 Vs^{-1} on the electrochemical response of ASA at the MWCNT-EP composite electrode was also investigated. It was found a linear increase of the peak currents with the square root of the scan rate (results are not presented here), with good correlation coefficients, which informed about a mass transport controlled oxidation process that is desired for the detection application. Moreover, during the scan rate increasing it was noticed more positive shifting of the oxidation peak potential, which confirms irreversibility of the oxidation process.

3.3. Determination of ASA in real samples

Based on the above-presented results, differential-pulsed voltammetry (DPV) technique has been employed to further investigate the electrochemical behavior of ASA at the MWCNT-EP

composite electrode. The potential usefulness of the DPV method for the determination of the ASA content in real sample solutions was verified using aqueous solutions of dissolved tablets of Aspirin (OZONE, Romania). Fig. 3a depicts a series of DPVs as examples involving ASA determination in an Aspirin real sample solution in 0.1 M Na_2SO_4 supporting electrolyte in the concentration range from 0.02 to 1.2 mM ASA. Calibration plots of anodic peak currents vs. ASA concentrations showed a very good sensitivity of 0.068 mA·mM^{-1} and a very good linearity with a correlation coefficient, R^2=0.999. The tested real sample example was prepared under the conditions mentioned in the experimental part and using a 0.594 g Aspirin tablet dissolved in 0.3 M NaOH and distilled water. A value of 485 mg ASA/tablet represented the average content determined using anodic DPV technique at MWCNT-EP composite electrode associated with standard addition method. The investigation of three Aspirin tablets with an average weight of 0.5946 g led to a value of 485 mg ASA/tablet. Each single tablet should contain 500 mg ASA in according to the general OZONE product specification,. The recovery degree of 97% indicates that this proposed method is effective for the determination of ASA and it exhibits a great potential for the practical applications in the detection of ASA in commercial samples.

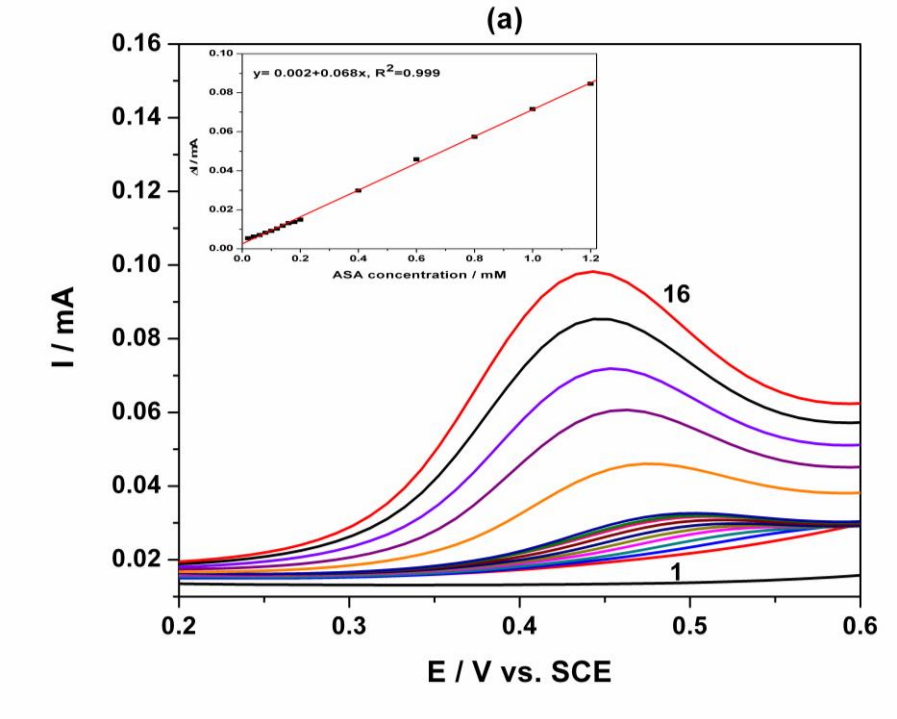

Figure 3a. DPVs of the MWCNT-EP composite electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) (0.1 V modulation amplitude, 0.01 V step potential), potential scan rate of 0.05 Vs^{-1} and in the presence of: 2) 0.02; 3) 0.04; 4) 0.06; 5) 0.08; 6) 0.1; 7) 0.12; 8) 0.14; 9) 0.16; 10) 0.18; 11) 0.2; 12) 0.4; 13) 0.6; 14) 0.8; 15) 1; 16) 1.2 mM ASA concentrations. Inset: the calibration plot of the anodic peak currents recorded at E= +0.44 V *vs.* ASA concentration.

Fig. 3b shows DPVs recorded under similar conditions using 0.1 M NaOH supporting electrolyte and a slight shifting to a lower potential value of the oxidation peak is noticed. Also, the sensitivity of 0.081 mA·mM^{-1} obtained using the 0.1 M NaOH supporting electrolyte is better in comparison with the 0.1 M Na_2SO_4 supporting electrolyte (0.068 mA·mM^{-1}).

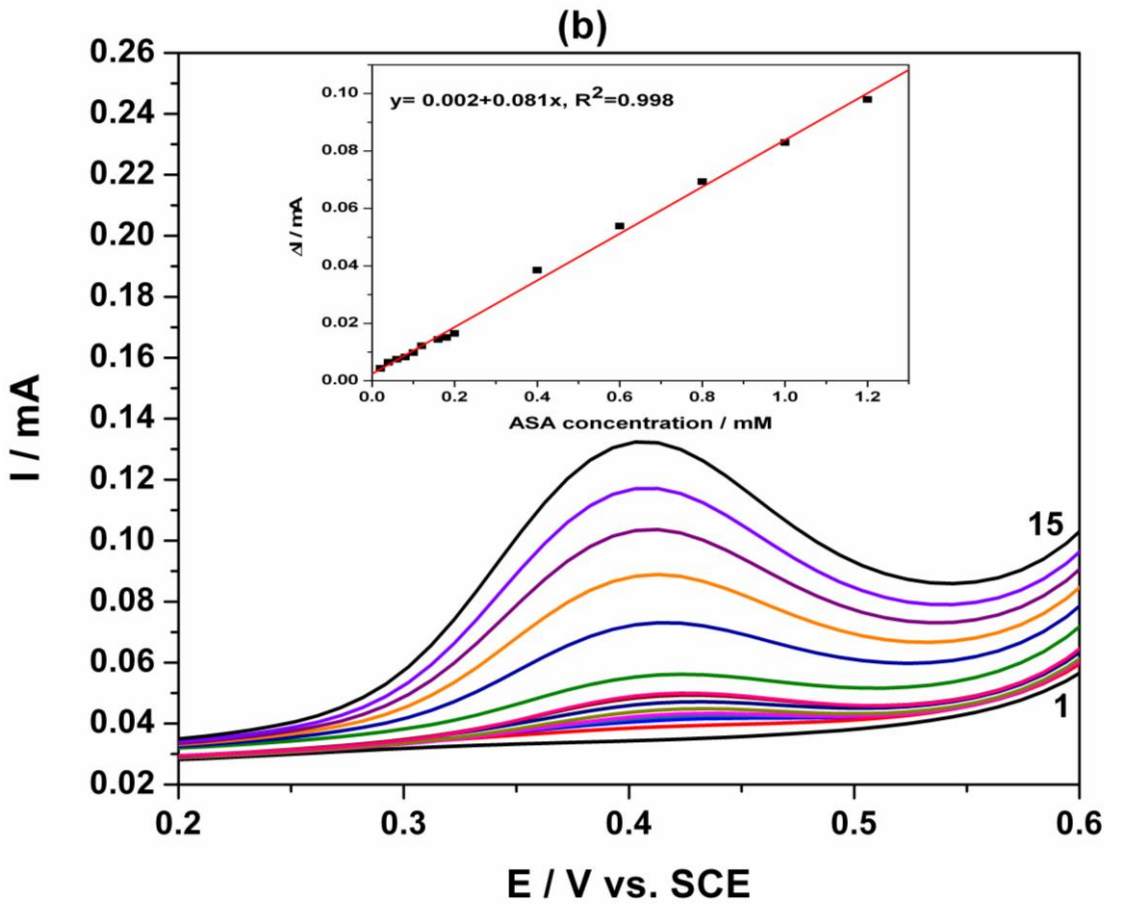

Figure 3b. DPVs of the MWCNT-EP composite electrode in 0.1 M NaOH supporting electrolyte (curve 1) (modulation amplitude 0.1 V, step potential 0.01 V), potential scan rate of 0.05 Vs^{-1} and in the presence of: 2) 0.02; 3) 0.04; 4) 0.06; 5) 0.08; 6) 0.1; 7) 0.12; 8) 0.16; 9) 0.18; 10) 0.2; 11) 0.4; 12) 0.6; 13) 0.8; 14) 1; 15) 1.2 mM ASA concentrations. Inset: the calibration plot of the anodic peak currents recorded at E= + 0.42 V *vs*. ASA concentration.

3.4. Chronoamperommetry measurements

The chronoamperometry (CA) is known as the easiest amperometric detection method that is very useful for the practical in-situ on in-field detection applications. Figs. 4a and 4b show CA measurements of ASA using the MWCNT-EP composite electrode under stationary conditions in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolyte solutions.. These figures represent the current-time profiles obtained by setting the working electrode at +0.55 V and +0.50 V vs. SCE, respectively, for various ASA concentrations. The useful current signals recorded after 50 seconds depended linearly on the ASA concentration within the concentration range from 0.2 mM to 1.2 mM. No fouling effect was noticed for the investigated concentration range.

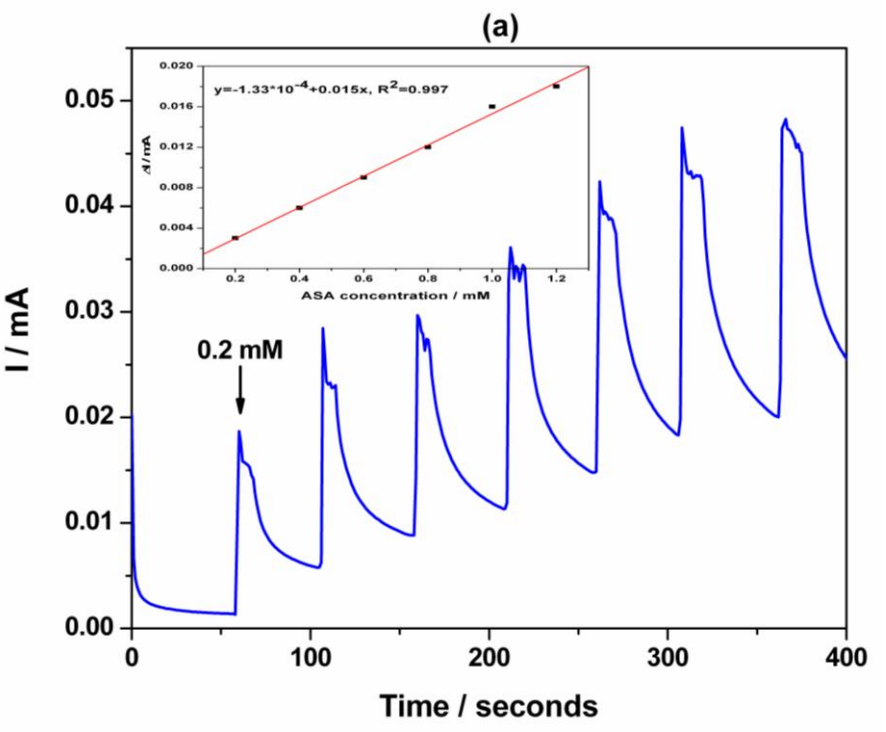

Figure 4a. CAs of the MWCNT-EP composite electrode in 0.1 M Na_2SO_4supporting electrolyte and in the presence of: 0.2, 0.4, 0.6, 0.8, 1, 1.2 mM ASA recorded at E= +0.55 V *vs.* ASA concentration.

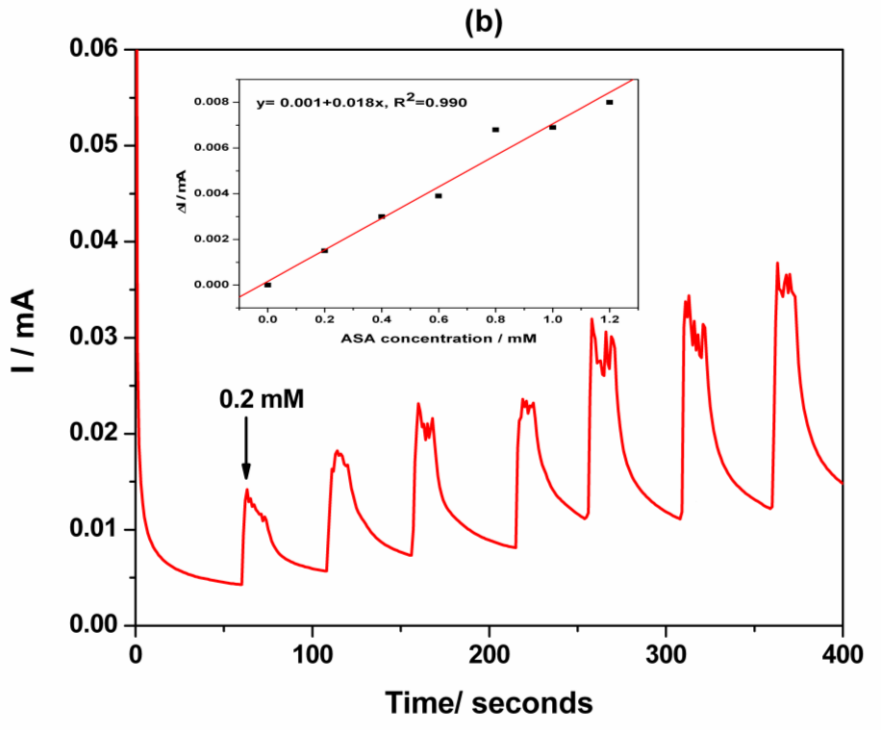

Figure 4b. CAs of the MWCNT-EP composite electrode in 0.1 M NaOH supporting electrolyte and in the presence of: 0.2, 0.4, 0.6, 0.8, 1, 1.2 mM ASA recorded at E= +0.50 V *vs.* ASA concentration.

The electroanalytical parameters for direct ASA detection using the MWCNT-EP composite electrode in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes are gathered in Table 2.

The limit of detection (LOD) was calculated as three times the standard deviations of intercepts (S_a) divided by the slopes of the regression lines (b), while the limit of quantification (LQ) value was estimated as ten times the standard deviation of intercepts (S_a) divided by the slopes of the regression line (b) [27, 28]. A good accuracy of the DPV-based electrochemical detection of ASA was found by comparison with UV-VIS spectrophotometric method.

Table 2. The electroanalytical parameters for direct detection of ASA using MWCNT-EP composite electrode in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes

Supporting electrolytes	Peak potential (V)	Technique used	Concentration range (mM)	Sensitivity ($mA \cdot mM^{-1}$)	Correlation coefficient (R^2)	LOD (mM)	LQ (mM)	RSD (%)
0.1 M Na_2SO_4	+ 0.55 V	CV	0.02-1.2	0.063	0.996	0.007	0.024	1.196
	+ 0.44 V	DPV	0.02-1.2	0.068	0.999	0.004	0.014	0.746
	+ 0.55 V	CA	0.2-1.2	0.015	0.997	0.040	0.138	4.878
0.1 M NaOH	+ 0.50 V	CV	0.02-0.2	0.054	0.994	0.008	0.028	1.120
	+ 0.42 V	DPV	0.02-1.2	0.081	0.998	0.005	0.018	0.434
	+ 0.50 V	CA	0.2-1.2	0.018	0.990	0.041	0.139	4.944

These results are very promising for the voltammetric/amperometric detection of ASA on the MWCNT-EP composite electrode. In comparison with other reported nanostructured carbon modified glassy carbon electrodes [18, 19] that exhibited very high electroanalytical performance, this electrode exhibits the advantage of stability, reproducibility and a very easy cleaning method by mechanical polishing. The electrode was tested after one year for a period of three years and the results are reproducible.

4. CONCLUSIONS

The MWCNT-EP composite electrode was successfully applied for the direct determination of ASA based on the electrocatalytic activity towards the oxidation of ASA with linear responses over a wide range of concentrations (from 0.02 to 1.2 mM). The electrochemical determination of ASA at the MWCNT-EP composite electrode was achieved using both 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolytes and employing CV, DPV and CA techniques. The alkaline medium did not improve significantly the sensitivity for ASA detection but the less positive oxidation potential shifting

in comparison with the neutral medium was noticed. Very good linearities of the calibration plots of anodic currents versus ASA concentrations resulted from all employed electrochemical techniques tested. The values of RSD ranged from 0.5 % to 5 % informed about a good reproducibility of this detection method. The MWCNT-EP composite electrode exhibited useful properties as environmentally friendly sensor for the electrochemical determination of ASA in relation with the atbility, life time, low cost, simple preparation, and easy renewal of the active electrode surface.

ACKNOWLEDGEMENTS
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References

1. D. Lawrence, *The Lancet* 360 (2002) 1003.
2. S. Weggen, M. Rogers and J. Eriksen , *Trends. Pharmacol. Sci.* 28 (2007) 536.
3. A.O. Maree, R.J. Curtin, M. Dooley, R.M. Conroy, P. Crean, D. Cox and D.J. Fitzgerald, *J. Am. Coll. Cardiol.* 47 (2005) 1258.
4. T.S. Poulsen, S.R. Kristensen, L. Korsholm, T. Haghfelt, B. Jørgensen, P.B. Licht and H. Mickley, *Thromb. Res.* 120 (2007) 477.
5. J. Cuzick, F. Otto, J.A. Baron, P.H. Brown, J. Burn, P. Greenwald, J. Jankowski, C.L. Vecchia, F. Meyskens, H.J. Senn and M. Thun, *Lancet Oncol.* 10 (2009) 501.
6. J. Rivera-Utrilla, M. Sanches-Polo, M.A. Ferro-Garcia and G. Prados-Joya, *Chemosphere* 93 (2013) 1268.
7. K.K. Verma and A. Jain, *Anal. Chem.* 58 (1986) 821.
8. Z. Kokot and K. Burda, *J. Pharm. Biomed. Anal.* 18 (1998) 871.
9. A.B. Moreira, I.L.T. Dias, G.O. Neto, E.A.G. Zagattoc, M.M.C. Ferreira and L.T. Kubota, *Talanta* 67 (2005) 65.
10. P.L. Janssen, M.B. Katan, P.C. Hollman and D.P. Venema, *J Agric. Food Chem.* 44 (1996) 1762.
11. A.W. Abu-Qare and M.B. Abou-Donia, *J. Pharm. Biomed. Anal.* 26 (2001) 939.
12. R. Szostak and S. Mazurek, *Analyst* 127 (2002) 144.
13. C. Wang, T.J. Vickers and C.K. Mann, *J. Pharm. Biomed. Anal.* 16 (1997) 87.
14. J.G. Nikelly, *Anal. Chem.* 36 (1964) 2248.
15. M.J. Scotter, D.P.T. Roberts, L.A. Wilson, F.A.C. Howard, J. Davis and N. Mansell, *Food Chem.* 105 (2007) 273.
16. V. Supalkova, J. Petrek, L. Havel, S. Krizkova, J. Petrlova, V. Adam, D. Potesil, P. Babula, M. Beklova, A. Horna and R. Kizek, *Sensors* 6 (2006) 1483.
17. C. Cofan and C. Radovan, *Internat. J. Electrochemistry* (2011), doi:10.4061/2011/451830.
18. T-.L. Lu and Y-.C. Tsai, *Sens. Actuators, B* 148 (2010) 590.
19. S. Kruanetr, P. Pollard, C. Fernandez and R. Prablu, *Int. J. Electrochem. Sci.* 9 (2014) 5699.
20. G. Liu, S.L. Riechers, M.C. Mellen and Y. Lin, *Electrochem. Commun.* 7 (2005) 1163.
21. A. Remes, A. Pop, F. Manea, A. Baciu, S.J. Picken and J. Schoonman, *Sensors* 12 (2012) 7033.
22. J. Yu, J.G. Shapter, M.R. Johnston, J.S. Quinton and J.J. Gooding, *Electrochim. Acta* 52 (2007) 6206.
23. J. Yu, J.G. Shapter, J.S. Quinton, M.R. Johnston and D.A. Beattie, *Phys. Chem. Chem. Phys.* 9 (2007) 510.

24. K.M. Roth, A.A. Yasseri, Z. Liu, R.B. Dabke, V. Malinovskii, K.-H. Schweikart, L. Yu, H. Tiznado, F. Zaera, J.S. Lindsey, W.G. Kuhr and D.F. Bocian, *J. Am. Chem. Soc.* 125 (2003) 505.
25. E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.* 101 (1979) 19.
26. S.J. Konopka and B. McDuffie, *Anal. Chem.* 42 (1970) 1741.
27. M.E. Swartz and I.S. Krull, *Analytical method development and validation* , Marcel Dekker, New York, 1997.
28. R. Jain, Vikas and J.A. Rather, *Colloids Surf. B: Biointerfaces* 82 (2011) 333.