ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Determination of Ascorbic Acid Based on Heterogeneous Carbon Sensors Modified with Carbon Nanotubes and Gold Nanoparticles.

Eda Mehmeti[1], Ahmet Hajrizi[1], Tahir Arbneshi[2], Kristina Žagar[3], Anchalee Samphao[4], and Kurt Kalcher[1]*.

[1]Institute of Chemistry, Analytical Chemistry, Karl-Franzens University of Graz, Graz, Austria.
[2]Department of Chemistry, Faculty of Natural Science, University of Prishtina, Prishtina, Kosovo.
[3]Department for Nanostructured Materials, Jozef Stefan Institute, Ljubljana, Slovenia.
[4]Department of Chemistry, Ubon Ratchathani University, Ubon Ratchathani, Thailand.

ABSTRACT

The effects of carbon nanotubes (CNTs) and gold nanoparticles (AuNPs) for the detection of ascorbic acid (AA) were elucidated and their performance as modifiers in carbon paste and screen printed carbon electrodes was compared to unmodified electrodes. The studies were made with cyclic voltammetry (CV) and flow injection analysis (FIA). As a supporting electrolyte 0.1 M phosphate buffer (pH 7.5) was used. The results show that in comparison to CNTs and AuNPs alone, the sensor modified with both nano-structured materials gives increased current signals at potentials where oxidation of AA occurs. The nature of the catalytic action of this combination as mediator is based on the huge surface of the nano-structured material. Screen printed carbon electrode (SPCE), modified with CNTs and AuNPs and phosphate buffer (pH 7.5) as a carrier were chosen for FIA with amperometric detection. The operating potential range was varied from +200 mV to -200 mV, where the favorable potential seemed to be +100 mV which gives high signals with the selected sensor system. The flow rate was tested from 0.1 to 0.8 mL/min and a value of 0.4 mL/min was chosen for subsequent analyses. A linear dependence of the peak current on the concentration of AA was observed within 1 to 200 mg/L with a correlation coefficient of 0.9986. The detection limit (3σ) was determined as 0.4 mg/L. The repeatability (4 measurements, 100 mg/L AA) was calculated as 5 %, the reproducibility (5 sensors, 100 mg/L AA), as 9 %.

Nevertheless, the results seem promising that the proposed sensor can be applied for quick estimations of the concentration of AA.

Keywords: carbon paste electrode, screen printed electrode, ascorbic acid, carbon nanotubes, gold nanoparticles, flow injection analysis

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Currently one of the most active areas of analytical research is the development of chemical sensors [1]. An important group of chemical sensors is based on electrochemical principles [2]. These sensors have found important applications in different analytical fields, such as clinical, environmental, industrial, and agricultural analysis. In electroanalysis, solid electrodes are frequently used based on carbon materials due to their advantages, such as broad potential window, low background current, rich surface chemistry, low cost, chemical inertness and suitability for various sensing and detection applications [3]. In 1958 Adams initially reported the use of carbon paste as an electrode material [4]. Carbon paste electrodes (CPEs) consist of a carbon powder in combination with a pasting liquid (organic binder). Currently screen-printing fabrication technology is well established for the mass production of thick film electrodes [5].

Modification of electrochemical sensors (electrodes) is an important feature to broaden the applicability of the devices and to increase specificity. Nowadays, nanoparticles are very interesting and useful modifiers for electrochemical sensors [6].

Since their discovery in 1991 by Iijima [7] carbon nanotubes (CNTs) play a huge role as modifiers in modern electroanalytical sciences. CNTs are allotropes of carbon, their main common forms are made by one or multiple cylindrical layers of graphene sheets (single-walled, SWCNT, and multi-walled, MWCNT) [8].

The specific characteristics of CNTs have promoted a large number of considerable applications in electroanalytical chemistry, including electrochemical sensors with an enlarged active surface area, which yields enhanced electrochemical responses, accompanied by an anti-fouling capability of electrode surfaces upon modification [9]. A CNT-modified electrode to study the oxidation of dopamine with bromoform as a binder was reported by Britto et al. in 1996 [10]. CNTs have then received enormous attention for the preparation of electrochemical sensors, as it was reviewed by Wang et al. [11, 13] and Hill et al. [12].

Nowadays, nano-sized particles of noble metals have attracted enormous interest, in particular gold nanoparticles (AuNPs), because of their attractive electronic, optical, and thermal properties, in addition to their catalytic effects and potential applications in some areas of medicine, chemistry, biology, physics and material sciences [14]. Their high surface energy makes them enormously reactive [15] and useful for the development of chemical sensors [16].

The gold compounds which are most commonly used as precursors for the generation of nanoparticles are auric trichloride ($AuCl_3$) and tetrochloroauric acid ($HAuCl_4$). Numerous methods to synthesize AuNPs, in particular with rather monodisperse size, have been reported and reviewed by several authors. The most frequently applied method was described first by Turkevich and Frens for the reduction of $HAuCl_4$ with citrate yielding particles with sizes of 10 to 150 nm [17, 18]. Another method for the synthesis of most hydrophobic AuNPs with diameter in 1 nm to 8 nm using sodium borohydride as a reducing agent in the presence of dodecanethiol was developed by Brust et al. [19, 20]. Hussain and co-workers synthesized AuNPs with different functional thiol ligands with a size less than 5 nm using thioethers or thiol-functionalized polymers [21].

Modification of the electrode surfaces is usually applied in order to improve the stability and the analytical performance of sensors [22].

Ascorbic acid (AA) is a soluble vitamin widely present in many biological systems. It plays also an important role in body health and is frequently used in food supplements as anti-oxidant. The existence of two neighboring hydroxyl groups in its structure facilitates easy oxidation to dehydroascorbic acid (DHA), a process which is influenced by many factors such as temperature, pH, oxygen, metals and enzymes [23]. Oxidation of AA at carbon electrodes has been well documented with numerous electrochemical methods with high working potentials [24]. For the electrochemical determination of this compound many modified electrodes have been developed and reported [25]. Xie and Dong described the electrocatalytic oxidation of AA at gold electrodes modified with bis(4-bipyridyl) disulfide [26]. Ascorbic acid could be also oxidized at electrodes modified with ruthenium(III)- diphenyldithiocarbamate as a mediator [27]. Yogeswaran reported a functionalized carbon nanotube-modified electrode for the simultaneous determination of ascorbic acid, epinephrine, and uric acid [28]. A graphene doped CPE was used for the successful determination of ascorbic

acid [29]. Typical samples to which these methods can be applied comprise beverages and pharmaceuticals [30].

In this work new electrochemical method will be presented for the determination of ascorbic acid using heterogeneous carbon electrodes. The aim was to develop an easy to use, reliable analytical procedure with very simple instrumentation for the electrochemical quantitation of the ascorbic acid with carbon paste and screen printed carbon electrodes. The most important advantage should be easy preparation of the electrode which makes the system functional in constructing simple sensors for the determination of the analyte. Furthermore, the effect of carbon nanotubes (CNTs) and/or gold nanoparticles (AuNPs) as modifiers for the graphite paste or ink composite should be elucidated with the focus on applying the resulting sensors directly to the analyses of samples without any further treatment.

EXPERIMENTAL

Chemicals and solutions

All reagents were of analytical grade and used without further purification. Deionized water was purified with a cartridge purification system (Milli-Q) to a resistivity of 18.2 MΩ cm and was used for all experiments.

Ascorbic acid, sodium dihydrogenphosphate dihydrate and disodium hydrogenphosphate dihydrate were purchased from Fluka (Buchs, Switzerland). Graphite powder, high purity grade (RW-C), was obtained from Ringsdorff Werke GMBH (Bonn- Bad Godesberg, Germany). Paraffin oil (Uvasol), tri-sodium citrate dihydrate and uric acid were purchased from Merck (Darmstadt, Germany). Multiwall carbon nanotubes (MWCNT) (o.d. 7-15 nm and tube length 0.5-10 µm), gold (III) chloride trihydrate ($HAuCl_4 \bullet 3H_2O$) and dopamine hydrochloride were supplied by Sigma-Aldrich (Wien, Austria). Hexadecanethiol and Triton X-100 were obtained from Fluka (Buchs, Switzerland). Carbon ink (Electrodag 421 SS) was purchased from Acheson (Scheemda, The Netherlands). Paracetamol ($C_8H_9NO_2$) originated from Genericon Pharma (Graz, Austria).

If not mentioned otherwise phosphate buffer solution (PBS, 0.1 M, pH 7.5) was used as supporting electrolyte; it was prepared by mixing corresponding amounts of NaH_2PO_4 and Na_2HPO_4 solutions (both 0.1 M) to achieve the desired pH. Stock solutions of ascorbic acid (200 mg/L; 100 mg/L) were prepared freshly each day by dissolving corresponding amounts of the analyte in PBS (0.1 M).

Commercial tablets of ascorbic acid (vitamin C) were purchased from Replek pharm (Skopje, Macedonia).

Apparatus

Cyclic voltammetric experiments were performed using an electrochemical analyzer (PalmSens, The Netherlands) controlled by a personal computer, using the necessary software (PSTrace, version1.2). The electrochemical cell consisted of a glass vessel (Metrohm) equipped with a carbon paste or a screen-printed working electrode (unmodified and modified). The reference electrode was an Ag/AgCl (3 M KCl, Metrohm 6.0733.100) and the auxiliary electrode a platinum wire. The pH was measured using a pH meter (models 210 A^+, Thermo Orion).

The system for flow injection analysis was set up from a peristaltic pump (model P-1, Pharmacia, Ealing, London), an injection block (Rheodyne 5020, Cotati, CA, USA) with a 100 µL loop and an electrochemical thin layer flow cell (spacer thickness 0.19 mm, CC5, BAS, West Lafayette, Indiana, USA) in combination with a potentiostat (100B, BAS) operated with the corresponding software (100W, version 2). The thin layer cell was equipped with the working electrode (CPE or SPCE, unmodified or modified) and an Ag/AgCl reference electrode (3 M KCl, BAS-RE-4) stored in 3 M KCl when not in use. The counter electrode was the steel plate of the electrochemical cell.

All potentials given in the text are versus the Ag/AgCl reference electrode.

Gold nanoparticle preparation

Gold nanoparticles were prepared similar to the literature [15, 31]. Briefly, 1 mL of a solution of gold(III) chloride trihydrate (4 mg/mL) were mixed with 18 mL of water and heated to a boil; then 2 mL of an aqueous solution of tri-sodium citrate dihydrate (1 % m/v) was slowly added as a reducing agent. The resulting mixture was stirred for 10-15 min after removing from the heating source and was allowed to cool to room temperature. Triton X-100 (20 µL) was added as a stabilizer. The resulting suspension was stored at 4 ºC. The size of the AuNPs was determined as 75 nm with a distribution range of 40-120 nm via the zeta potential (Zetasizer Nano S, Malvern Instruments, Worcestershire, UK) and by transmission electron microscopy.

Working electrodes

Carbon paste electrodes

Plain carbon paste was prepared by carefully hand mixing 380 µL of paraffin oil with 1.0 g of graphite powder in a mortar with a pestle. After standing overnight a portion of the resulting paste was packed into the end of a Teflon tube (an inner diameter 6.90 mm, outer diameter 10.15 mm) and the surface was polished using a PTFE plate or wet filter paper. Whenever regeneration was required, a layer of the surface was removed and replaced by fresh paste. Electrical contact was made with a copper wire through the center of the tube.

Screen printed electrodes

Plain screen printed electrodes were prepared on pre-etched ceramic substrates (Coors Ceramic GmBH, 113x166x0.635 mm alumina plate, No.CLS 641000396R) with carbon ink using a semi-automatic printing device (SP-200, MPM, Franklin, MA, USA). The stencil had a thickness of 100 µm and produced 30 sensors with a sensing area 35x3 mm in one run. After printing the electrode plates were dried at room temperature and then broken into individual sensors. Silver conductive paint was applied on one end of the SPCE, to which a crocodile clamp was attached for electrical contact.

Modification

Modification with carbon nanotubes was done by simply adding the modifier to the carbon paste and the printing ink, respectively (5 % m/m).

Modification with gold nanoparticles was done by adding 60 µL of hexadecanethiol to the carbon paste and printing ink. After that gold nanoparticles were attached to the electrode surface (unmodified or modified with CNTs) by exposing the electrode to the nanoparticle solution for six hours.

Procedures

Cyclic voltammetry

For cyclic voltammetry measurements the supporting electrolyte (20.0 mL) was transferred into the voltammetric cell and deaerated with high purity argon (99.99 %) for 5 min before the measurements. Then the voltammograms were recorded in a potential range between -0.6 V and +0.6 V with a scan rate of 50 mV/s. Usually 5 cycles were registered.

Flow injection analyses

Flow injection analysis (FIA) was performed with the following parameters: injection volume: 100 µL; flow rate: 0.4 mL/min; operating potential +100 mV (if not mentioned otherwise). After attaining a stable baseline injection of the analyte was launched. The signals were evaluated as peak heights.

ISSN: 0975-8585

Interferences

The interferences of uric acid, paracetamol and dopamine which may occur in biological samples were measured in FIA mode in concentrations of 20, 100 and 500 mg/L. Before each injection of an interferent solution, ascorbic acid (100 mg/L) was injected and measured.

Samples

Vitamin C tablets were powdered, and an aliquot (0.13 g) was extracted three times with 20.0 mL of phosphate buffer solution and filtered in a glass filter crucible (G3); the combined filtrates were made up to 100 mL with PBS. The concentration of ascorbic acid was determined by FIA with external standards and with standard addition.

For reference determinations extraction was performed analogously by using water instead of PBS. Before filling up to 100 mL final volume, 15 mL of sulphuric acid (1 M) were added. After addition of 1 mL of starch solution (1 % m/v) aliquots were titrated with standardized iodine solution [32].

RESULT AND DISCUSSION

Cyclic voltammetry

Preliminary experiments to explore the activity of the unmodified and modified electrodes toward AA were tested with cyclic voltammetry. Figure 1 shows cyclic voltammograms of 200 mg/L AA in phosphate buffer solution (pH 7.5) recorded with unmodified and modified carbon-paste electrodes in the potential range of -0.6 to +0.6 V.

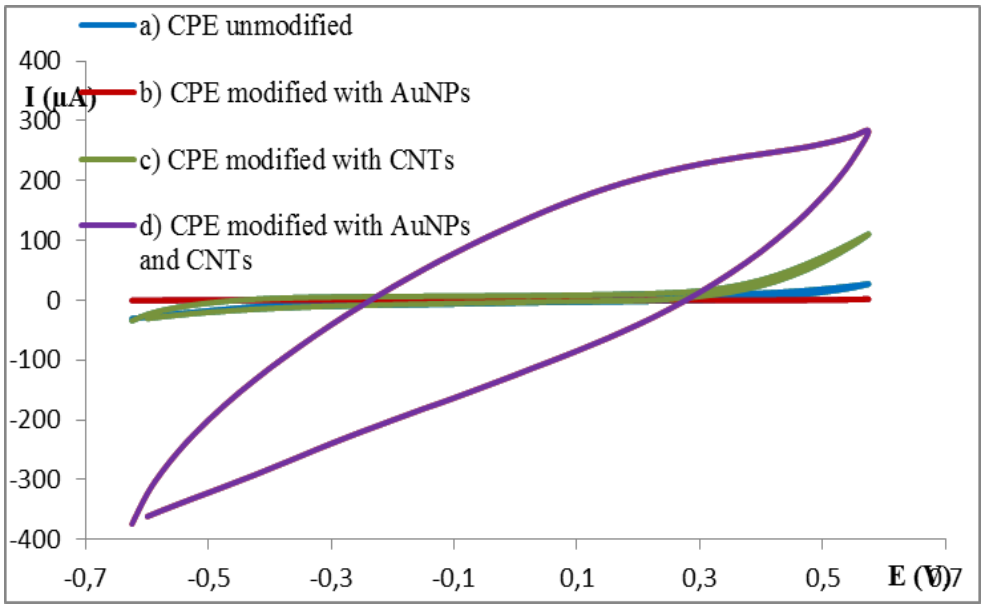

Figure 1: Cyclic voltammograms of 200 mg/L ascorbic acid at CPEs; a) the unmodified carbon paste electrode; b) modified carbon paste with gold nanoparticles; c) modified carbon paste with carbon nanotubes; d) modified carbon paste with carbon nanotubes and gold nanoparticles; at pH 7.5 in 0.1 M phosphate buffer; at scan rate of 50 mV/s.

Ascorbic acid undergoes notable oxidation at the surface of the unmodified carbon paste electrode at potentials higher than 0.2 V. The oxidation to dehydroascorbic acid seems irreversible at CPEs because no pronounced reduction signal can be observed in the negative potential range (a).

A further approach to detect AA more specifically was made by modification of the electrode surface with gold nanoparticles (particle size 35 to 75 nm), which were attached to the electrode by hexadecanethiol, present in the electrode bulk (b). The effects caused by ascorbic acid are rather small in the positive, as well as

in the negative potential range. In a next step the influence of carbon nanotubes on the electrochemical behavior of ascorbic acid was investigated (c). The anodic currents were higher than with the unmodified electrode. Nevertheless significant oxidation occurs at potentials higher than 0.2 V. Reduction of the analyte at negative potentials is practically not observable. When comparing the cyclic voltammograms of the different carbon paste electrodes, gold nanoparticles do not show an improving effect; in contrast the currents are decreased compared to the unmodified electrode. Carbon nanotubes seem to improve the signal height to some extent. The last design of the sensor for ascorbic acid was based on modification with both, CNTs and AuNPs to see if a synergistic effect occurs. The cyclic voltammogram shows very high currents in the presence of ascorbic acid (Fig.1, curve d) which cannot be simply interpreted as an additive effect of the modifiers. Clearly, the high currents result from a synergism of both nanosized materials.

Compared to carbon paste electrodes, screen-printed carbon electrodes (SPCEs) are mechanically more robust, better storable, and easier to use as a simple sensor. They exhibit usually higher background currents, and require more time-consuming steps for their preparation. In order to see if SPCEs are superior to CPEs, they were modified in the same way as the carbon paste electrodes and investigated in the same supporting electrolyte (Fig. 2).

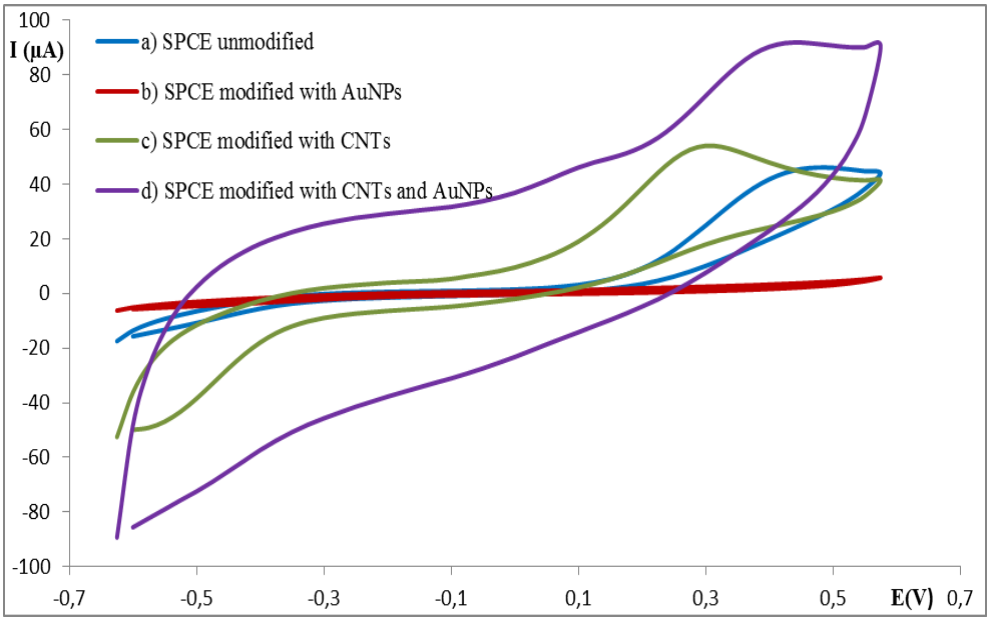

Figure 2: Cyclic voltammograms of 200 mg/L ascorbic acid at SPCEs; a) the unmodified screen printed carbon electrode; b) modified screen printed carbon electrode with gold nanoparticles; c) modified screen printed carbon electrode with carbon nanotubes; d) modified screen printed carbon electrode with carbon nanotubes and gold nanoparticles; at pH 7.5 in 0.1 M phosphate buffer; at scan rate of 50 mV/s.

In general, the electrochemical signals are much better manifested in the voltammograms than with carbon paste electrodes. The plain screen printed carbon electrode (curve a) shows oxidation of ascorbic acid as a peak at around 0.4 V. Practically no reductions occur in the reverse scan. When modifying SPCEs with AuNPs (curve b) the cyclic voltammograms show different behavior than the unmodified sensors. In the investigated medium the peak-like shape of the oxidation current of AA is lost, and only small oxidation signals can be seen at rather positive potentials. The reason could be the modification of the bulk electrode material with thiol, and maybe a surface modification caused by Triton X 100, which had been used as a stabilizer for the AuNPs. When modifying SPCEs with CNTs c), the oxidation potential is lowered to 0.3 V compared to the unmodified electrode and the peak like shape is well established. At even negative potentials reduction currents can be seen. Finally again a synergistic effect between CNTs and AuNPs could be observed by modifying SPCEs with both nanomaterials. High oxidation currents occur beyond 0.2 V, superimposed on a rather high background. When comparing the cyclic voltammograms of ascorbic acid at different modified electrodes, it can be found that CNTs exert a catalytic effect on the oxidation of ascorbic acid resulting in a decrease of the oxidation potential. AuNPs alone, at least under the experimental conditions applied here,

show a negative effect by decreasing the oxidation current and eliminating peak-shaped signals at least in the potential range investigated.

The combination of CNTs and AuNPs causes a high background current, but also increases the oxidation current to some extent. Again, the oxidation signal shows a peak-like shape. The nature of catalytic action of CNTs and CNTs in combination with AuNPs is still not completely elucidated, but is certainly based on the huge surface of the nonostructured material. Due to the latter, the electron transfer proceeds more easily via CNTs which causes a decrease of the oxidation potential.

Flow injection analysis (FIA)

Comparison between CPEs and SPCEs

In this work, a FIA procedure with the amperometric detection for the determination of ascorbic acid is proposed using carbon paste electrodes and screen printed carbon electrodes, both unmodified and modified with CNTs and AuNPs.

The current flow was monitored in dependence of time, and the signals in FIA are typically transient with time. When the plug of the analyte solution is injected into the carrier it is transported towards the detector. At the boundary layers dispersion due to diffusion occurs so that the shape of the signal typically shows the form of a peak. Phosphate buffer (0.1 M, pH 7.5) was used as carrier solutions, with a flow rate of 0.4 mL/min with the injection volume of AA 100 µL. The effect of several parameters on the amperometric response of AA under flow injection conditions using CPEs and SPCEs was investigated in order to optimize the FIA parameters.

Figure 3 summarizes the dependence of the peak current of ascorbic acid in FIA mode on the operating potential for CPEs using phosphate buffer solution (pH 7.5) as a carrier.

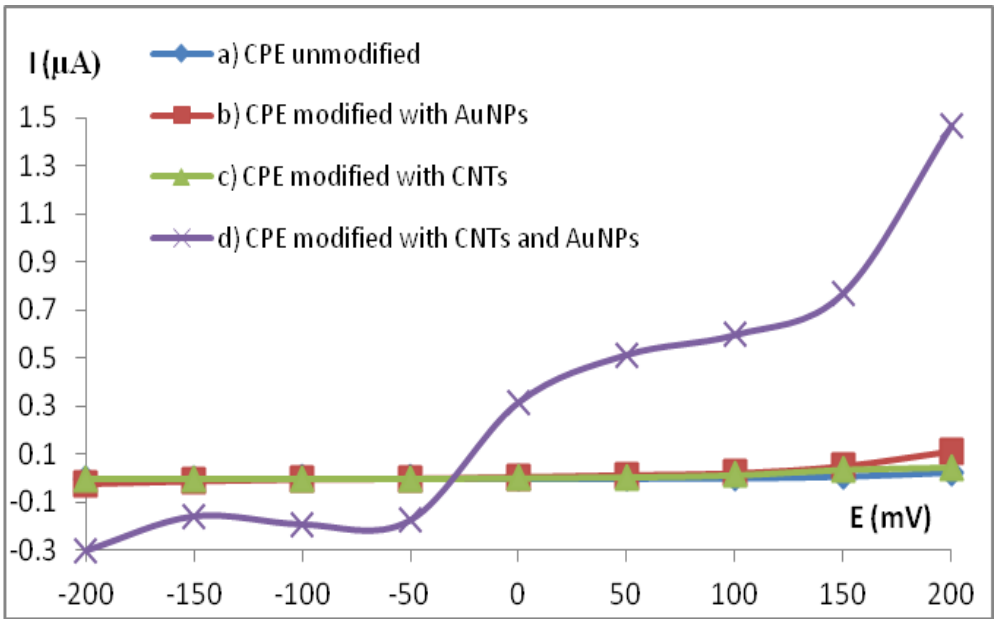

Figure 3: Dependence of the peak height of AA on the operating potentials with CPE electrodes, flow rate 0.4 mL/min, 0.1 M phosphate buffer pH 7.5 as a carrier, injection volume 100 µL of AA in concentration of 100 mg/L.

As can be seen the plain electrode gives rather small oxidation signals at positive potentials (curve a). The electrode modified with AuNPs (curve b) gives significantly higher, but still small responses in the positive potential range. CNTs alone (curve c) increase the oxidation current of ascorbic acid at potentials > 100 mV, but to a lesser extent. The modified electrode with both modifiers (curve d) shows the best performance by yielding oxidation currents at 0 V and beyond, again as a synergistic effect between the nanomaterials.

ISSN: 0975-8585

In Figure 4 the dependence of the signal of ascorbic acid in FIA mode on the operating potential is summarized for SPCEs using phosphate buffer solution (pH 7.5) as a carrier.

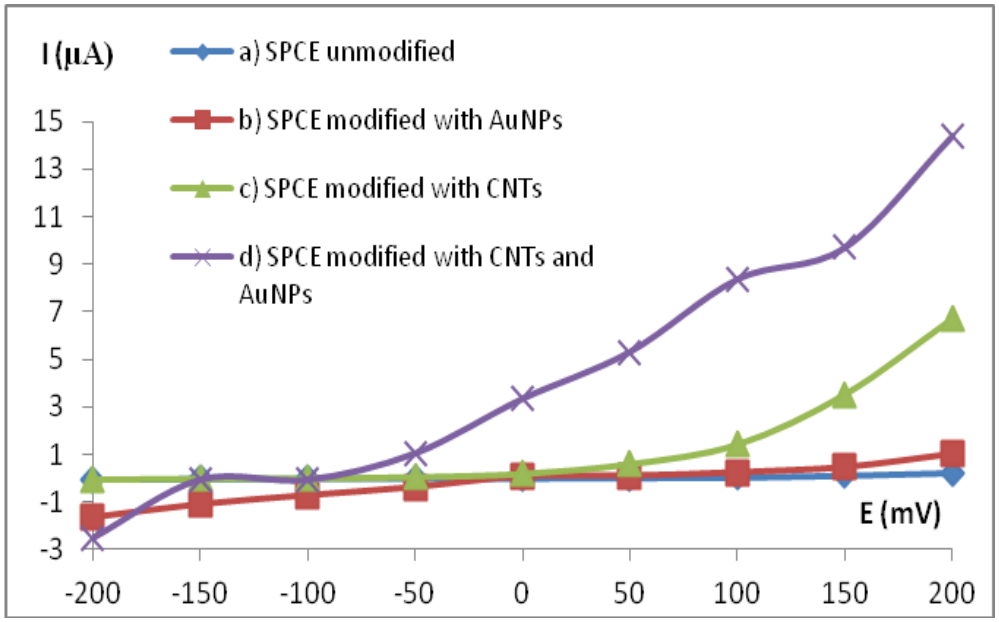

Figure 4: Dependence of the peak height of AA on the operating potentials with SPCE electrodes, flow rate 0.4 mL/min, 0.1 M phosphate buffer pH 7.5 as a carrier, injection volume 100 µL of AA in concentration of 100 mg/L.

Ascorbic acid shows low signals with the unmodified electrode (curve a). AuNPs (curve b) only slightly improve the responses. With CNTs (curve c) a significant increase of the oxidation current at positive potentials occurs. The combined effect of CNTs and AuNPs (curve d) on the oxidation of ascorbic acid is very dominant which can be monitored at -50 mV already. Also in the negative potential range significant catalytic improvements of the signal can be observed with CNTs and AuNPs as modifiers.

When comparing the results of the amperometric detection of ascorbic acid with FIA it is prominent that the combined catalytic effect of CNTs and AuNPs is present with carbon paste and screen printed electrodes. CNTs show a significant effect with SPCEs, which is amplified by AuNPs. When comparing the current densities of SPCEs and CPEs (ratio of area of SPCE:CPE = 4:1) the thick film electrodes usually give higher responses than the carbon paste sensors under otherwise identical conditions. This may be due to the more hydrophilic surface of the former compared to the latter.

Studies were also performed with other media with different pH, namely acetic acid-acetate buffer (pH 4.5) and ammonia-ammonium chloride buffer (pH 9.5). The former one gave in general signals which were smaller than with phosphate buffer. NH_3/NH_4Cl as a medium caused generally increased signals for carbon paste surfaces (but still less than for SPCEs), whereas the responses at screen printed electrodes were significantly lower than in phosphate buffer. Therefore phosphate buffer was used as the medium of choice for further analytical investigations.

Analytical Procedure with SPCEs

From the results shown above it can be concluded that screen-printed electrodes modified with CNTs and AuNPs provide best results. Therefore, this system was chosen for further investigations. With respect to the operating potential, +100 mV was selected because it is reasonably low (lower risk for co-oxidation of other components in complex matrices) but still gives high signals with the selected sensor system. The flow rate was optimized in the range 0.1 to 0.8 mL/min and did not show high variations, but appeared almost constant from 0.3 to 0.8 mL/min with very slight decrease only. Also at slower flows, a slight decrease could be observed the reason for which is unclear because an opposite trend would be expected. For subsequent analyses a flow rate of 0.4 mL/min was chosen. Figure 5 shows a typical amperogram of ascorbic acid with the modified screen printed carbon electrode as a detector.

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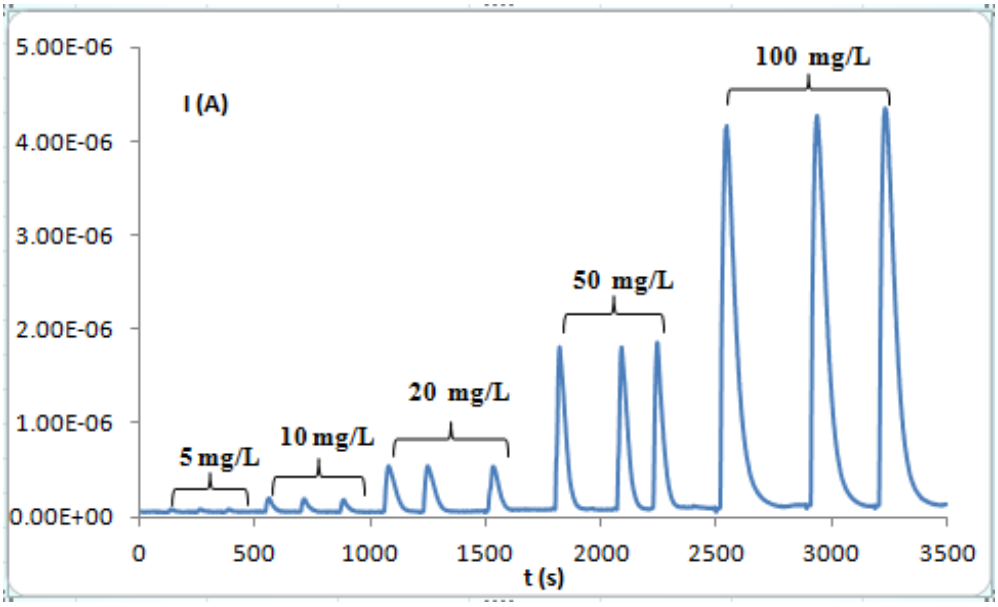

Figure 5: Flow injection amperogram recorded with SPCEs modified with AuNP and CNT; flow rate 0.4 mL/min, carrier 0.1 M phosphate buffer (pH 7.5); working potential +100 mV.

Figure 6 illustrates a calibration curve for ascorbic acid as obtained with screen printed carbon electrodes modified with carbon nanotubes and gold nanoparticles. The graph is linear within a concentration range from 1 to 200 mg/L with a correlation coefficient of R^2 equal to 0.9986. The detection limit (3σ) was estimated as 0.4 mg/L. The repeatability (n = 4 measurements, c = 100 mg/L ascorbic acid) was calculated as 5 % RSD, the reproducibility (n = 5 sensors, c = 100 mg/L ascorbic acid) as 9 %.

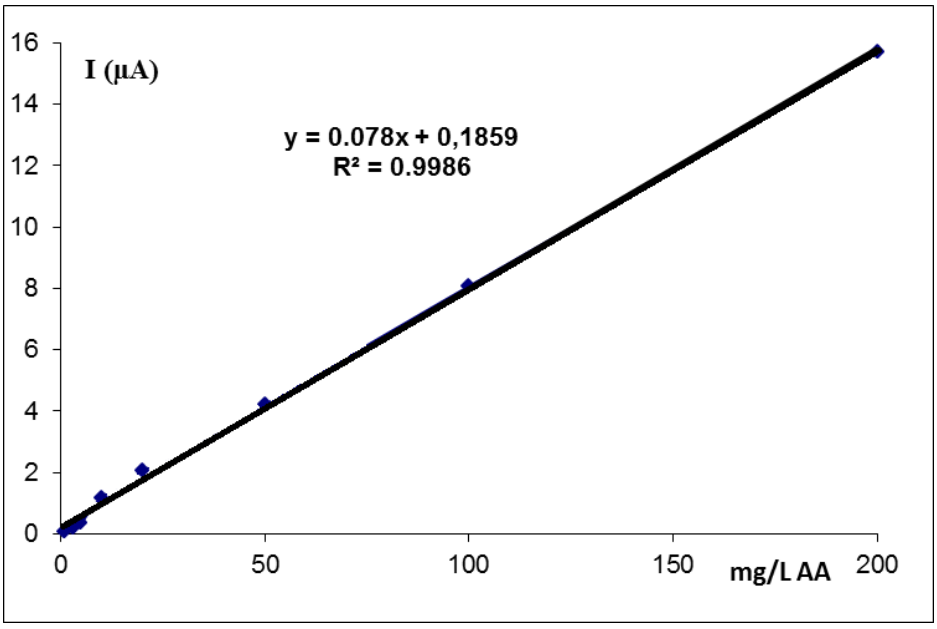

Figure 6: Calibration curve for various concentration of ascorbic acid (1-200 mg/L) at SPCE modified with CNTs and AuNPs, at applied working potential + 100 mV vs.Ag/AgCl, flow rate 0.4 mL/min; carrier solution phosphate buffer (pH 7.5)

To validate the specificity of the SPCE modified with CNTs and AuNPs for the determination of AA, common interferents such as uric acid, dopamine and paracetamol which may occur in biological samples were tested.

ISSN: 0975-8585

Uric acid and paracetamol do not give notable signals under the optimized experimental conditions; only dopamine shows an oxidation current which is less than 5 % compared to the signal of AA (100 mg/L) if its mass concentration is a fifth of the concentration of the analyte (20 mg/L), but increases almost linearly to about 60 % with a concentration of 500 mg/L.

Sample

The proposed FIA procedure with the CNTs/AuNPs-modified screen printed carbon sensor was applied to the determination of ascorbic acid in a pharmaceutical formulation (Table 1). The AA content was determined by the standard addition method (Figure 7) and compared with that obtained by the official method (iodometric titration) according to the Pharmacopoea Jugoslavica [32]. The mean value of the concentration obtained by the calibration curve corresponds quite well to the value obtained by the official method. The standard deviations of the electrochemical determinations (SD) are significantly higher. The results are confirming that there are no significant differences between the results obtained and seems promising that the sensor can be applied for quick estimations of the concentration of ascorbic acid in such formulations.

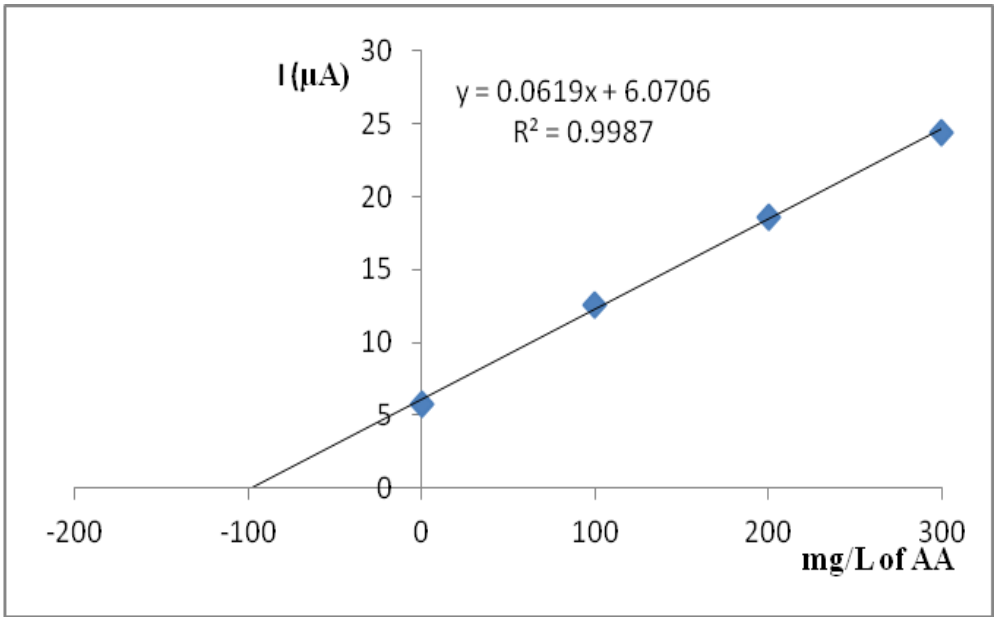

Figure 7: Calibration curve of ascorbic acid in tested tablets as obtained with standard addition in FIA mode; in 0.1 M phosphate buffer as carrier solution; flow rate 0.4 mL/min; operation potential + 100 mV; injection volume 100 µL with the SPCE modified with CNTs and AuNPs.

Table 1: Mean results obtained for the determination of ascorbic acid in pharmaceutical formulations by FIA amperometric procedure in comparison with the official method [32].

	content (mg per tablet)
nominal value	500
FIA (calibration curve)	503 ± 9
FIA (standard addition)	504 ± 10
Reference method	499 ± 0.4

Table 2 shows a comparison of the proposed sensor with other electrodes described in the literature. The method presented in this work has a good linearity range and detection limit. Some modified electrodes have lower detection limits; nevertheless, the sensor described in this paper seems to be more suitable for determination of ascorbic acid in pharmaceutical preparations because due to the nature of the sample very low detection limits are not required.

ISSN: 0975-8585

Table 2. Electrochemical sensors for the determination of ascorbic acid.

Electrodes	Modifiers	Method	Limit of Detection (LOD) mg/L	Linearity Range mg/L	Ref.
GCE	polyaniline doped with silicotungstic acid and carbon nanotubes	Amperometry	0.09	1.8 - 1580	[33]
CPE	multiwalled carbon nanotubes, ionic liquid, and palladium nanoparticles	Differential pulse voltammetry	0.035	0.1-20	[34]
GCE	reduced graphene oxide	Differential pulse voltammetry	0.12	0.12 - 17.6	[35]
GCE	Carbon-Spheres	Differential pulse voltammetry	0.11	52.8 - 352	[36]
CPE	Silver nanoparticle and carbon nanotube (Ag/CNT–CPE)	Differential pulse voltammetry	2.1	5.3-352	[37]
SPCE	Carbon nanotubes and Gold nanoparticles (CNTs/AuNPs)	Flow injection analysis	0.4	1-200	This work

CONCLUSIONS

This work demonstrates the use of heterogeneous carbon sensors, based on carbon paste and screen printed sensors, modified with CNTs and AuNPs, for the determination of ascorbic acid. The study presented here showed that CNTs and AuNPs, particularly in combination, may improve the voltammetric and the amperometric behavior of ascorbic acid at heterogeneous carbon electrodes. From the point of view of sample throughput rate and analysis time, FIA seems preferential over voltammetry. Comparing carbon paste and screen-printed electrodes the latter is superior over the former with respect to signal heights and mechanical stability. It was shown that screen-printed electrodes modified with CNTs and AuNPs can be useful sensors for quick determination of ascorbic acid, as demonstrated with a pharmaceutical vitamin C preparate.

ACKNOWLEDGMENTS

E.M. wishes to thank the financial support for this work from the ÖAD-Büro für Austauschprogramme, Österreichische Rektorkonferenz and World University Service-Graz, Austria. Support of the CEEPUS program (project **CII-CZ-0212-02-0809-M-28727)** is kindly acknowledged as well.

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