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Electrochemical Sensor for Determination of *L*-Cysteine Based on Carbon Electrodes Modified with Ru(III) Schiff Base Complex, Carbon Nanotubes and Nafion

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A new low potential electrochemical sensor for determination of *L*-cysteine based on carbon electrodes modified with Ru(III) Schiff base complex, multi-walled carbon nanotubes and Nafion is presented. Cyclic voltammetry, differential pulse voltammetry and flow injection analysis were employed. Measurements were carried out using Britton-Robinson buffer (pH 5.50). The results showed that addition of multi-walled carbon nanotubes to Ru(III) complex modified glassy carbon and screen printed carbon electrodes gives increased current signals at the potential where oxidation of *L*-cysteine occurs. Flow injection amperometric measurements were performed at the operating potential +0.15 V *vs.* Ag/AgCl (3 M KCl) electrode and showed fast electric current response for *L*-cysteine oxidation, demonstrating good reproducibility and stability. The sensor has a detection limit of 0.11 mg L^{-1} and a dynamic range of 50-500 mg L^{-1}. The repeatability was calculated as 2.8 %. New sensor was used for the determination of *L*-cysteine in pharmaceutical products.

Keywords: *L*-Cysteine, Ru(III) Schiff base complex, multi-wall carbon nanotubes, modified glassy carbon and screen printed carbon electrodes, voltammetric and amperometric determination

1. INTRODUCTION

L-cysteine (CySH) is a sulfur containing non-essential amino acid. The sulfhydryl group of CySH plays an important role in the biological activity of protein and enzymes. Biological functions of CySH as detoxifying and immunological competence agent and growth promoter are well described. Cysteine also plays and important role in diagnosis of cancer, Parkinson and Alzheimer diseases and acquired immune deficiency syndrome [1,2]. Deficiency of CySH induces retarded growth, hair depigmentation and liver damage [3]. There are several pharmaceutical applications of CySH such as: (i) it is a component of some antibiotics, (ii) is used for the treatment of skin damage and (iii) as a biomarker.

Due to large significance of CySH great efforts are being made to develop sensitive, simple, fast and easily available methods for its determination, that do not need technical training and extensive sample preparation. Several analytical methods are permanently in use: flow injection [4,5], high-performance liquid chromatography (HPLC) [6,7], colorimetry [8], chemiluminescence [9], spectrofluorimetry [10] and electrochemistry [11-16]. Electrochemical sensors accommodate all demands of good analytical methods.

Finding suitable electron transfer mediators for fast and low potential determination of CySH is of huge importance, since the direct oxidation of thiols at solid electrodes is very slow and requires at least +1.00 V potential [17, 18]. Several inorganic compounds, such as Prussian blue [19], copper hexacyanoferrate [20] and aquacobalamine [21] were used. Main problems in determination of CySH showed to be fouling of electron surface due to formation of different oxidation products at high potentials, low selectivity and sensitivity, high working potentials and narrow linearity range.

Over the last decades ruthenium complexes are subject of great interest since they showed excellent biological [22,23], catalytic [24] and electron-transfer mediating [25] properties. Ruthenium Schiff base complexes showed several key features as good mediators in development of electrochemical sensors: (i) thermodynamically stability, (ii) redox reversibility, (iii) excellent electron-transfer mediating properties, (iv) insolubility in water. Advantages of Ru(III) Schiff base complexes compared to other inorganic mediators are: (i) reduction in activation overpotential, (ii) decrease in surface fouling, (iii) high potential for formation of non-conducting oxide.

Here we describe rapid, simple, sensitive and reliable electrochemical determination of CySH in pharmaceutical products using glassy carbon and screen-printed carbon electrodes modified by sodium dichlorobis[*N*-phenyl-5-bromosalicylideneiminato-*N*,*O*]ruthenat(III)complex, hereinafter Na[$RuCl_2L_2$] (Fig. 1), multi wall carbon nanotubes and Nafion.

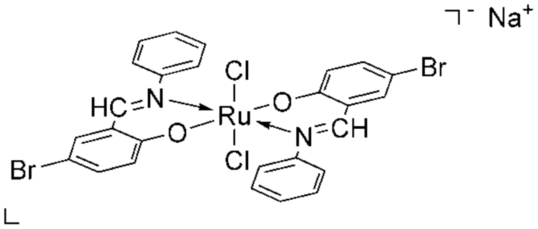


Figure 1. The structure of Na[$RuCl_2L_2$]

2. EXPERIMENTAL

2.1. Materials

Anionic Ru(III) Schiff base complex, Na[$RuCl_2L_2$] was synthetized according to published procedure and precipitated as sodium salt [26,27]. Purity was checked by CHN analysis and IR spectrum. Multi wall carbon nanotubes (95 %, 10 – 20 nm, 1 μm length) were supplied from Nanolab (Waltham, MA). A stock solution of 5 % Nafion in a mixture of lower aliphatic alcohols and water was obtained from Sigma-Aldrich (USA). A 1 % Nafion solution was prepared by diluting the Nafion stock solution with ethanol. All chemicals were of analytical grade and obtained from Sigma-Aldrich.

A phosphate buffer solution (0.10 M) was prepared by mixing appropriate volumes of the aqueous solutions of $NaH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 2H_2O$. Britton-Robinson buffer solutions (BRBS) were prepared by mixing 0.040 M acetic acid, 0.040 M phosphoric acid, and 0.040 M boric acid. Initial pH of 1.81 was adjusted with 0.2 M NaOH. Stock solutions of CySH (1000 mg L^{-1}) were freshly prepared using previously deaerated buffer by bubbling high purity argon gas (99.995%, Messer Griesheim, Gumpoldskirchen, Austria). Doubly distilled water was used in all experiments.

2.2. Electrode preparation

$Na[RuCl_2L_2]$ (2.50 mg) was dissolved in ethanol (125 μL), MWCNTs (2.00 mg) and Nafion solution (10 μL, 1%) were added. The mixture was sonicated for 30 minutes in an ultrasonic bath (PHYWE Ultraschall-generator) to improve the homogeneity. The black mixture was immediately used for electrode preparation.

Modified screen printed electrodes were prepared by dropping the modification mixture (10 μL) onto the previously defined carbon active area (35 × 4 mm) on porcelain plates (Coors Ceramic GmbH, Chattanooga, TN, USA) and air-dried for 1 hour at room temperature.

Glassy carbon electrode was mechanically polished with 1 - 0.05 μm α-alumina powder and cleaned ultrasonically with acetone and water. The modification mixture was dropped onto the GCE (0.28 cm^2 surface area) and then air-dried.

2.3. Methods

The electrochemical experiments were performed using an Autolab Potentiostat/Galvanostat (PGSTAT 12) with a standard three-electrode system. The system was run by PC through Autolab software (GPES, Version 4.8). Acidity was measured using pH-meter ISKRA (MA 5740). All potentials are given versus the Ag/AgCl reference electrode at room temperature. The results obtained were presented using the scientific graphing software SigmaPlot11.

Cyclic voltammograms (3 cycles) of CySH were recorded using 5 mL electrode cell in potential range 0.00 to +0.80 V applying scan rate from 75 to 250 mV s^{-1} in BRBS pH 5.50 using (un)modified GCE as working, platinum wire as counter and Ag/AgCl as reference electrode.

Differential pulse voltammograms of CySH were recorded in flow system in potential range 0.00 to +1.00 V applying scan rate of 20 mV s^{-1} in BRBS pH 5.50, pulse time of 0.05 s, pulse amplitude 0.025 V at flow rate 0.40 mL min^{-1} using modified SPCE as working, back plate of the flow cell as counter and Ag/AgCl (3M KCl, BAS RE-1) as reference electrode.

Amperometric analysis of CySH was carried out using flow injection system that consisted of a high performance liquid chromatographic (HPLC) pump (Model 510, Waters, Milford, MA, USA), a sample injection valve (U6K, Waters), and a thin-layer electrochemical cell (CC5, BAS Bioanalytical Systems Inc., West Lafayette IN, USA). Teflon spacers (MF-1047, MF-1048, BAS) were used to adjust the thickness of the flow-through cell. Measurements were performed at ooperating potential of +0.15 V, flow rate 0.40 mL min^{-1} using BRBS pH 5.50 as carrier with modified SPCE as working, back plate of the flow cell as counter and Ag/AgCl (3M KCl, BAS RE-1) as reference electrode.

2.4. Real sample preparation

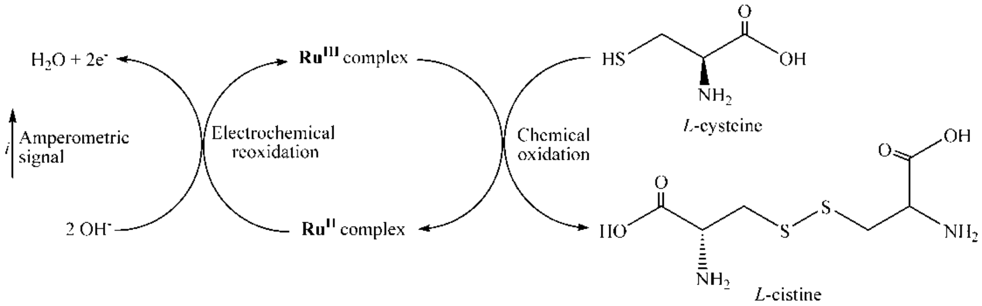
Two samples (Sample 1 and 2) were capsules from Kyberg Vital, Germany (450 mg *L*-Cysteine), and Gall Pharma, Austria (500 mg *L*-Cysteine), respectively. The content of the capsules was dissolved in 25.00 mL of BRBS, pH 5.50, and diluted prior analysis to required concentrations. Quantification was carried using FIA method.

3. RESULTS AND DISCUSSION

The studies were done using unmodified and Na[RuCl$_2$L$_2$]/MWCNT/Nafion modified SPC and GC electrodes. The response of the modified SPCE was optimized with respect to applied potential, flow rate and the pH of the solution. MWCNTs are carbon nanoparticle with multifunctional properties. Their remarkable nanostructure, which combines high electrical conductivity, high surface area, mechanical strength and good chemical stability showed to be of great importance in electroanalysis. We used MWCNTs for modification since they increase electroactive surface of electrode thus improving the response.

3.1. Cyclovoltammetric measurements

Cyclovoltammetry was used to demonstrate mediating properties of complex and to prove that oxidation of cysteine on modified GCE occurs. Oxidation of CySH on a bare GCE and a modified GCE was investigated in the potential range between 0.00 and +0.80 V at scan rate of 100 mV s^{-1}. Typical cyclic voltammograms are shown in Fig. 2. Oxidation of CySH on a bare carbon electrode requires a high positive potential as reported previously [22, 28]. The bare GCE in buffer solution displays no redox peaks in the investigated potential range (Fig. 2 curves a and b, respectively). On the modified GCE, a well-defined anodic peak appears at +0.48 V which is significantly increased after the addition of CySH (Fig. 2 curve d). This increase in anodic current can be attribute to good mediating properties of Na[RuCl$_2$L$_2$], along with high conductivity and large surface area of MWCNTs. Oxidation of CySH on the surface of solid electrodes is shown on Scheme 1.



Scheme 1. Oxidation of *L*-cysteine oxidation on the surface of modified solid electrode

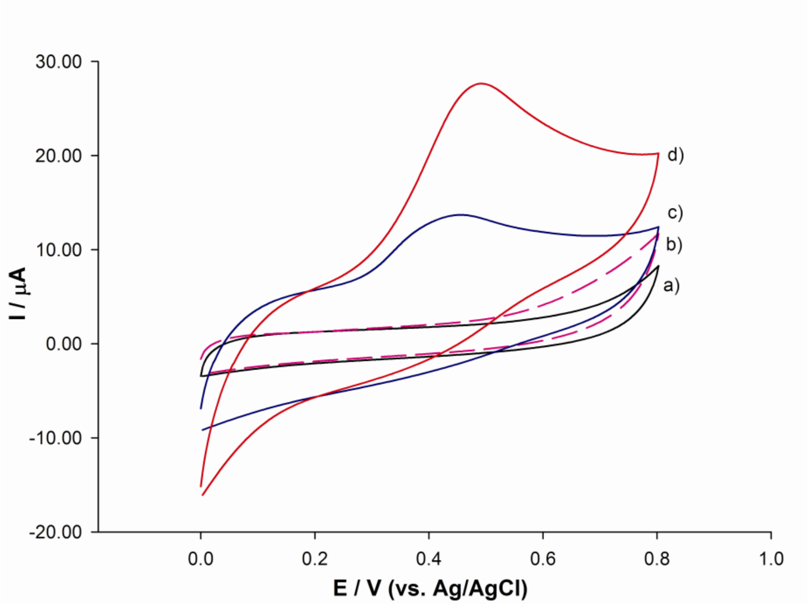


Figure 2. Cyclic voltammograms in the BR buffer (pH 5.50) with (a) an unmodified GC electrode, (b) an unmodified electrode with 45 mg L^{-1} CySH, (c) a modified GC electrode (d) a modified GC electrode with 45 mg L^{-1} CySH. Scan rate: 100 mV s^{-1}

Furthermore, cyclovoltammetry was used to investigate nature of electrochemical process. Fig. 3A illustrates the cyclic voltammograms of modified glassy carbon electrode at different scan rates (75 - 250 mV s^{-1}). CySH is irreversibly oxidized and Fig. 3B displays the plots of peak current versus square root of scan rate for CySH with a correlation coefficient 0.9976. This behavior is characteristic of diffusion-controlled processes [29]. However, the relationship between the redox peak current and the scan rate can be expressed as a power-law type as it follows [30, 31]:

$$I_{p,\,a} = kv^{x} \qquad (1)$$

$$\log I_{p,\,a} = \log k + x \log v \qquad (2)$$

where $I_{p,a}$ is the peak oxidation current density (mA cm^{-2}), v scan rate (mV s^{-1}), k proportionality constant and x is an exponent of scan rate. In the case that electrode kinetics meets (1), the electrochemical redox reaction is under the electron transfer process control, where x = 1, or the reactant diffusion process, where x = 0.5. Oxidation current density (log $I_{p,a}$) as a function of the scan rate (log v) (Fig. 3C) shows linear relationship (R^2 = 0.9948) in the range of 75 – 250 mV s^{-1}. The exponent of the scan rate x is found to be 0.817 which may indicate that the electron transfer process was also a limiting factor. This can occur if additional processes take place, such as increasing internal resistance due to contamination of the electrode with oxidation products of CySH and restricting movement through inner and outer Helmholtz plane.

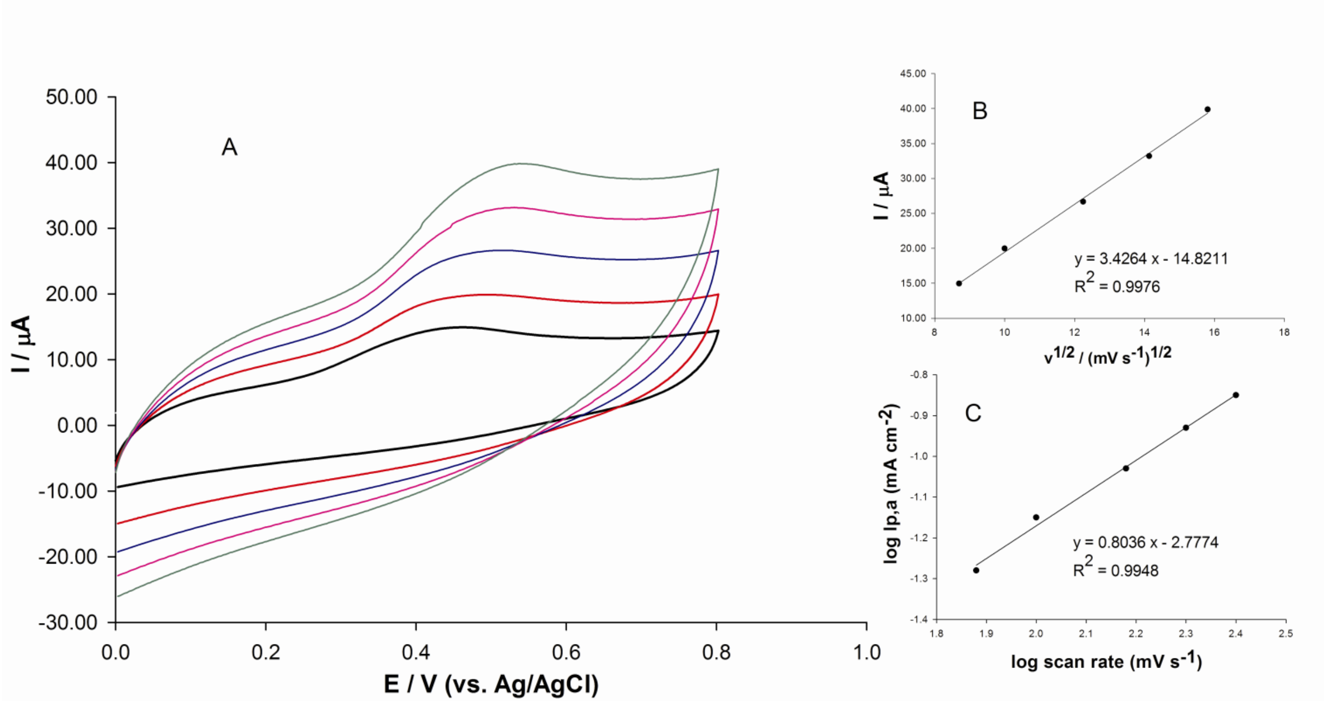


Figure 3. (A) Cyclic voltammograms of the CySH electrochemical oxidation at a $\mathrm{Na[RuCl_2L_2]}$/MWCNT/Nafion/GC electrode in BR buffer (pH 5.50) containing 20 mg L^{-1} CySH at different scan rates: 75-250 mV s^{-1}. (B) Dependence of current peak with the square root of scan rate. (C) Linear relation between log current anodic peak *vs.* log scan rates

3.2. Differential pulse voltammetry

Since cyclovoltammetry did not provide positive linear dependence of current response to concentration of CySH, differential pulse voltammetry was applied to confirm the effect. It was found that increase of CySH concentration results with decrease of oxidation peak current, suggesting an incomplete electrochemical response due to contamination of the electrode with oxidation products of CySH. Adsorption of the CySH and CyS-SCy on solid electrode surface blocks active sites of the modified electrodes thus making measurements unreliable [32, 33]. Oxidation of CySH on a solid electrode may proceed via the following reactions [34]:

$$\mathrm{CySH} \leftrightarrow \mathrm{CyS^-} + \mathrm{H^+} \qquad (3)$$
$$\mathrm{CyS^-} \rightarrow \mathrm{CyS^*_{ads}} + e^- \qquad (4)$$
$$2\ \mathrm{CyS^*_{ads}} \rightarrow \mathrm{CySSCy} \qquad (5)$$

Problem of chemisorbing cystine and its oxidized products such as cysteinesulfinic acid and cysteic acid was successfully eliminated using DPV in flow system where the carrier elutes the electrode surface thus preventing it from fouling of electrode.

As shown in Fig. 4A, increase of CySH concentration causes increase of oxidation peak current suggesting a good electrochemical response of the modified electrode. Dependence of CySH concentration versus anodic current response is given by linear regression i (μA) = 0.5498 [CySH] (mg L^{-1}) + 4.9490, R^2 = 0.9952 (Fig. 4B). Oxidation potential was found to shift negatively when using DPV in flow system (~0.50 V) compared to DPV in a stationary state (~0.60 V), which may be due to leaching of oxidized products on the electrode surface.

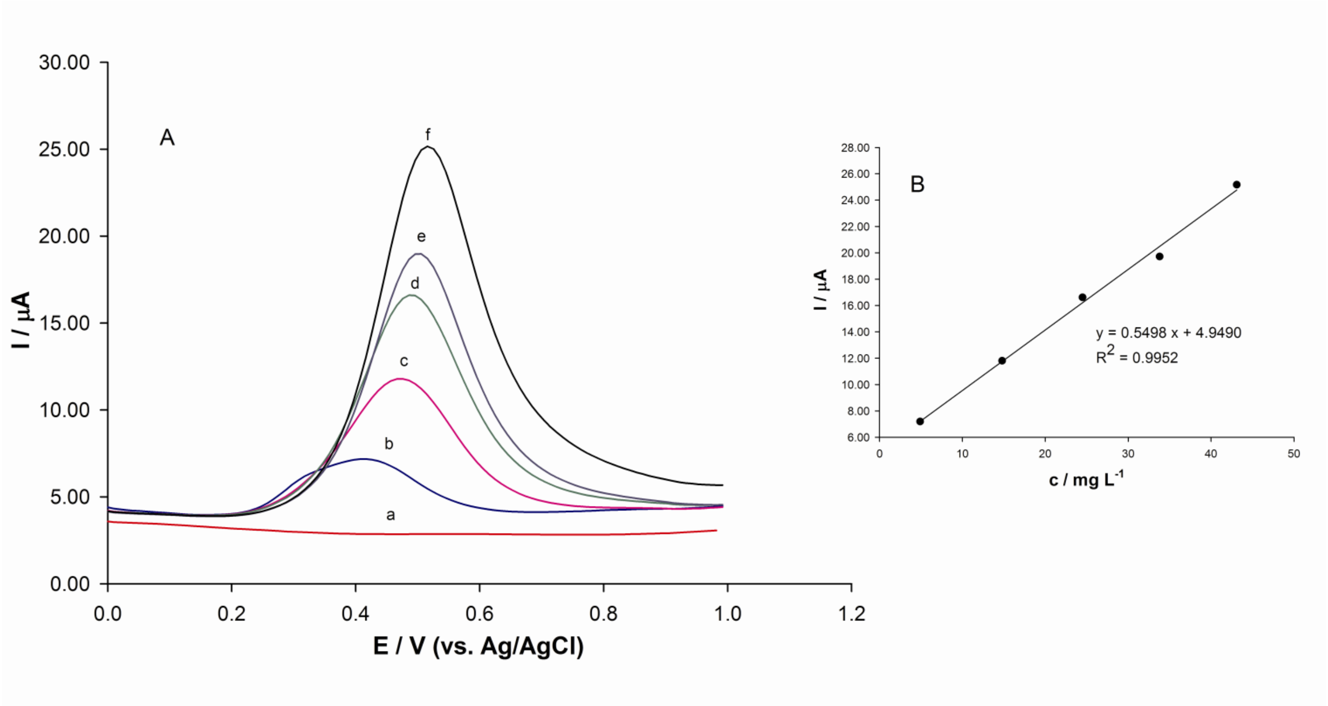


Figure 4. (A) Differential pulse voltammograms in flow system of CySH in BR buffer (pH 5.50) at modified GCE for different CySH concentrations (mg L^{-1}): (a) 0; (b) 4.90; (c) 14.80; (d) 24.50; (e) 33.80; (f) 43.10. Scan rate: 20 mV s^{-1}. (B) Plot of the peak current as a function of CySH concentration

3.3. Flow-Injection Analysis (FIA) amperometric measurements

Considering that oxidation products of CySH adsorb on the electrode surface, it is necessary to frequently clean the electrode or use the system with a flow of buffer over the electrode. In order to develop a simple and more sensitive procedure for the determination of *L*-cysteine FIA amperometry technique was employed. For FIA amperometry measurements, a modified $Na[RuCl_2L_2]$/MWCNT/Nafion/SPCE electrode was used.

Fig. 5 illustrates that the Ru(III) Schiff base complex showed an excellent mediating effect on the oxidation of CySH when used with MWCNTs and Nafion on screen printed carbon electrode. MWCNTs have good catalytic effects owing to their high surface activity and electron conductivity. Current peak heights corresponding to the different CySH concentrations clearly demonstrating fast and reproducible response of the new sensor. Amperometric determination is based on electrochemical oxidation of CySH on the SPCE, surface modified with Na[$RuCl_2L_2$]/MWCNT/Nafion.

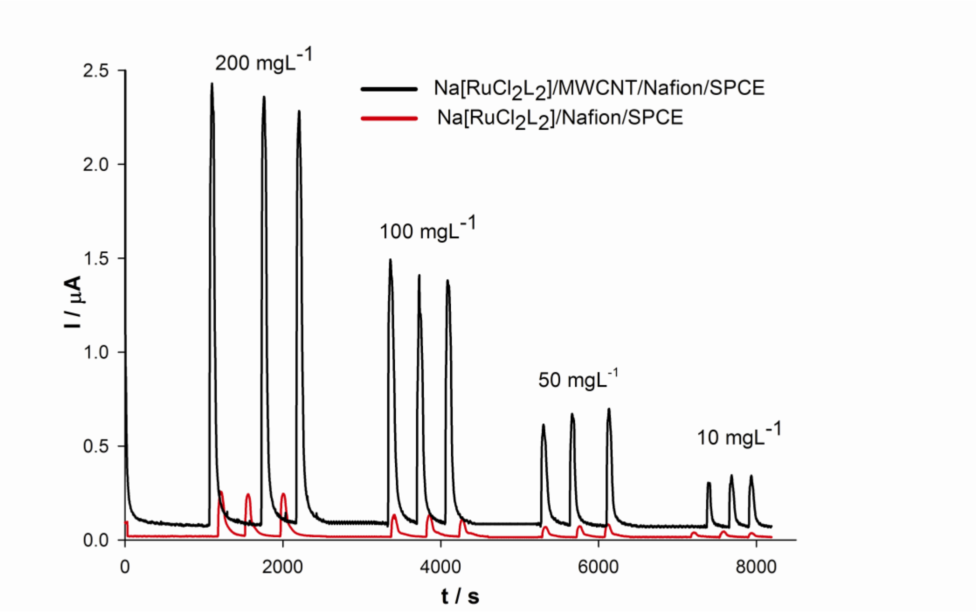


Figure 5. Amperometric FI response of CySH at a Na[$RuCl_2L_2$]/MWCNT/Nafion/SPCE (—), and a Na[$RuCl_2L_2$]/Nafion/SPCE (—), operating potential +0.15 V *vs*. Ag/AgCl, BR buffer (pH 5.50), flow rate 0.40 mL min^{-1}, injection volume 250 µL

3.4. FIA parameter optimization

3.4.1. Operating potential

The operating potential is a crucial parameter for amperometric response. Fig. 6 shows the dependence of of the background current (a) and the current response for 200 mg L^{-1} of CySH at applied potential from -0.20 to +0.40 V in BR buffer (pH = 5.50) with a flow rate of 0.40 mL min^{-1}.

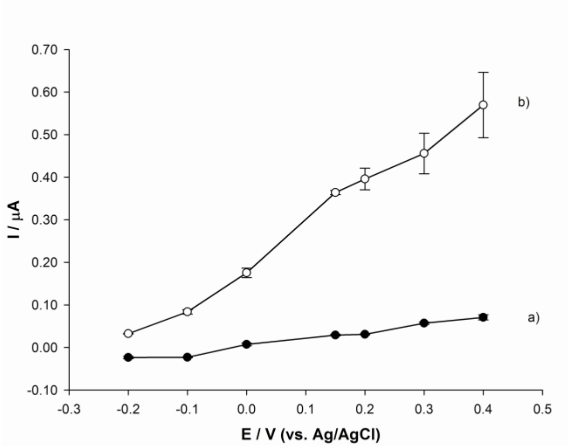


Figure 6. Dependence of the FI peak current response at modified SPCE on the applied potential: (a) background current, (b) current response for 200 mg L^{-1} of CySH. Working conditions: flow rate 0.40 mL min^{-1}, carrier BR buffer (pH 5.50), injection volume: 100 µL

The FIA current response increases upon increasing potential towards more positive values. Highly positive potentials are not suitable so electrodes modified with mediators, that reduce the overpotential of the analyte, have practical applicability. A working potential of +0.15 V was chosen for subsequent measurements because this potential is low enough to reduce appearing of interferences in real samples to a minimum. Standard deviation of peak height is also minimal. The potential of +0.15 V is significantly lower than the potentials that have been used previously [35].

3.4.2. Flow rate

As with any measurement in flow injection analysis, the amperometric signal is affected by the flow rate. A typical curve shown in Fig. 7 describes the dependence of FIA signal on the flow rate of the carrier for 200 mg L^{-1} of CySH. The current response exhibits an inverse relationship with the flow rate, the higher the flow rate the lower the current response. This is expected, since lower flow rates subsequently cause longer contact of the CySH with the surface of the modified electrode producing higher peak current. The flow rate of 0.40 mL min^{-1} was chosen as the most suitable for further experiments because it reduces analysis time and current response is satisfactory.

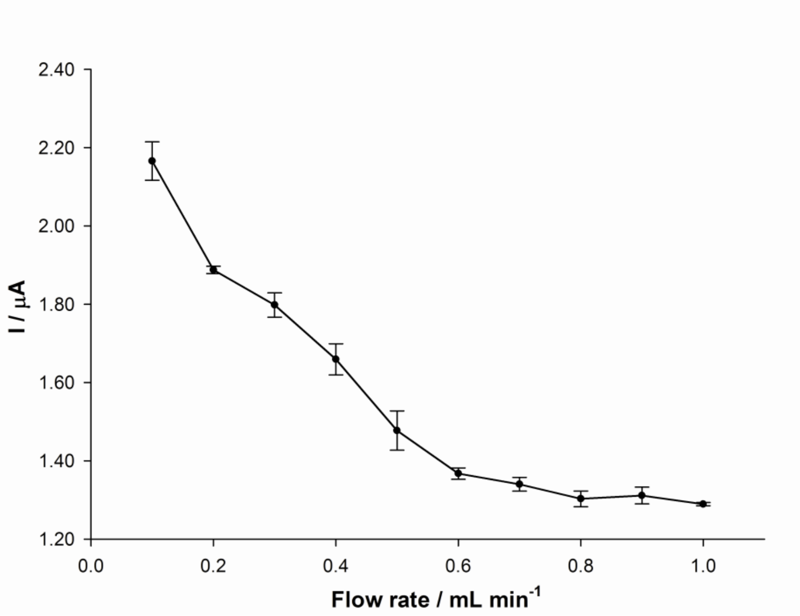
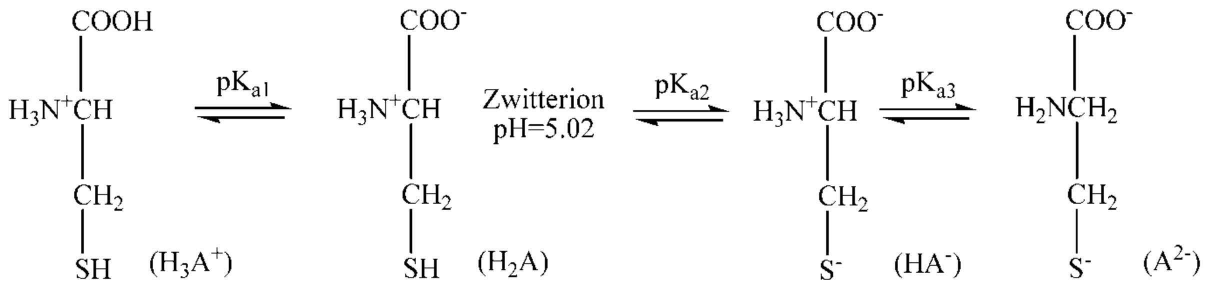


Figure 7. Dependence of the FIA peak current response at $Na[RuCl_2L_2]$/MWCNT/SPCE on the flow rate of the carrier. Operating potential +0.15 V, carrier BR buffer (pH 5.50), injection volume 250 µL, CySH 200 mg L^{-1}

3.4.3. pH of the carrier

The pH of the electrolyte influences the response of the electrode in the analysis of CySH, since different redox reactions of CySH can occur via interaction of CySH functional groups (-COOH pK_a 1.29, -SH pK_a 8.37 and $–NH_2$ pK_a 10.70) and $Na[RuCl_2L_2]$ as mediator at the electrode surface at different pH. Ionization of CySH can be described as follows [2]:



The electrochemical behavior of CySH was studied in 0.1 M phosphate and BR buffer at different pH values (from 3.50 to 9.00). It was found that oxidation of CySH on surface modified electrode increases with increasing pH value regardless to buffer used (Fig. 8). In alkaline conditions thiol group is deprotonated rendering oxidation more effective. However, alkaline solutions cannot be used since spontaneous oxidation of CySH occurs thus giving unreproducible and unreliable results. Compared to phosphate buffer better, more reproducible and repeatable current response was found in a BRBS. Therefore BRBS (pH 5.50) was chosen for further work.

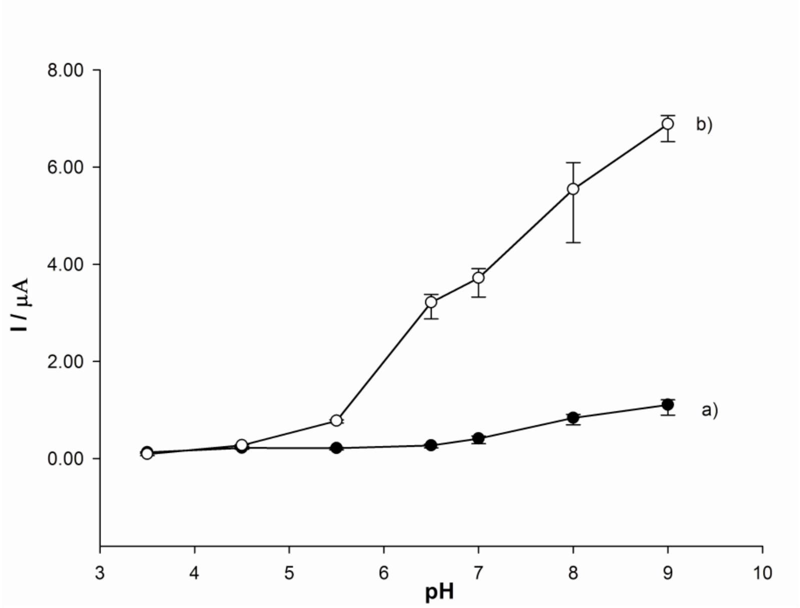


Figure 8. Dependence of the current response for 200 mg L^{-1} of CySH at $Na[RuCl_2L_2]$/MWCNT/Nafion/SPCE on the pH of the carrier. Operating potential +0.15 V, flow rate: 0.40 mL min^{-1}, injection volume 100 µL a) 0.10 M phosphate buffer b) BR buffer

3.5. Linearity, limit of detection and reproducibility

Linear relation between the amperometric peak current and concentration was found in the concentration interval from 50 to 500 mg L^{-1} CySH in a BR buffer (pH 5.50): i (µA) = 7.1900 [CySH] (mg L^{-1}) + 0.6077, R^2= 0.9868. Concentrations above 500 mg L^{-1} slightly deviate from linearity (Fig. 9B). Fig. 9A shows a typical amperogram for different concentration of CySH using $Na[RuCl_2L_2]$/MWCNT/Nafion/SPCE as detector. The limit of detection (LOD) was calculated from equation (3 s/m), where s is the standard deviation of FIA peaks (n=3) at 1 mg L^{-1} CySH and m is the slope of the calibration plot (Fig. 10). LOD were calculated as 0.11 mg L^{-1}. The repeatability (n=4 measurements, 25 mg L^{-1} CySH) was calculated as 2.8 %.

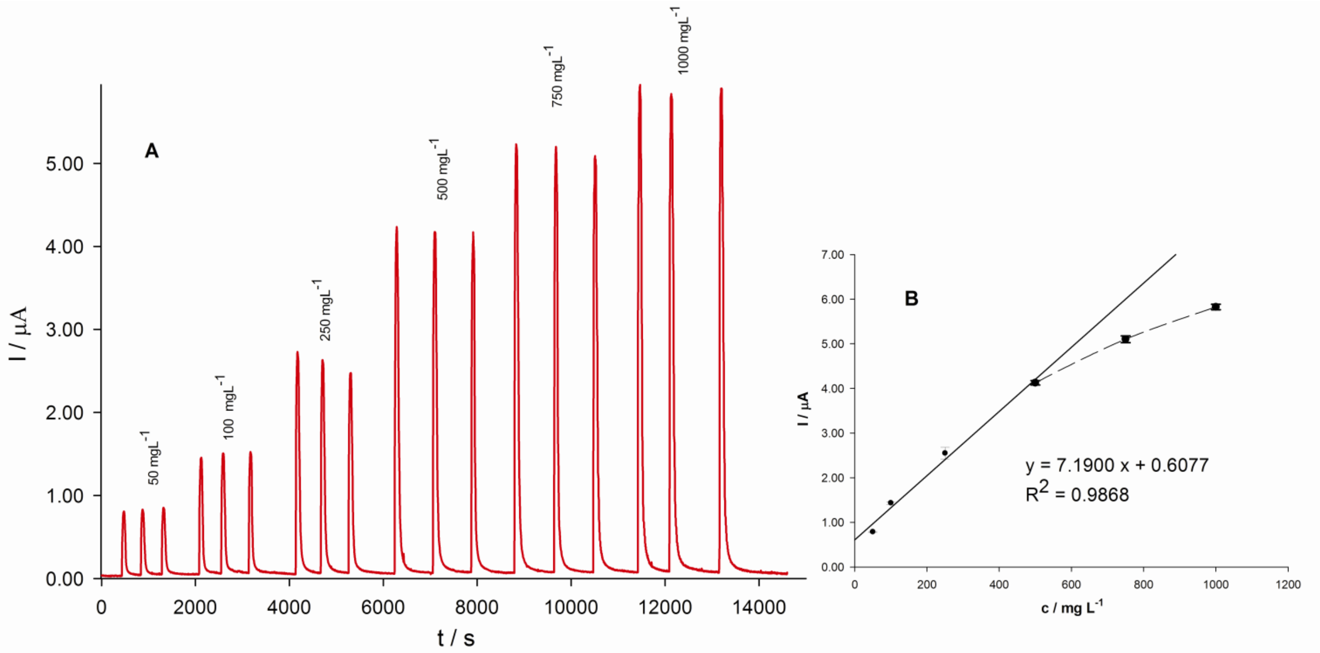


Figure 9. (A) Amperometric FI response of CySH at a Na[RuCl$_2$L$_2$]/MWCNT/Nafion/SPCE, operating potential +0.15 V *vs*. Ag/AgCl, BR buffer (pH 5.50), flow rate 0.40 mL min^{-1}, injection volume 250 μL; (B) Calibration curve

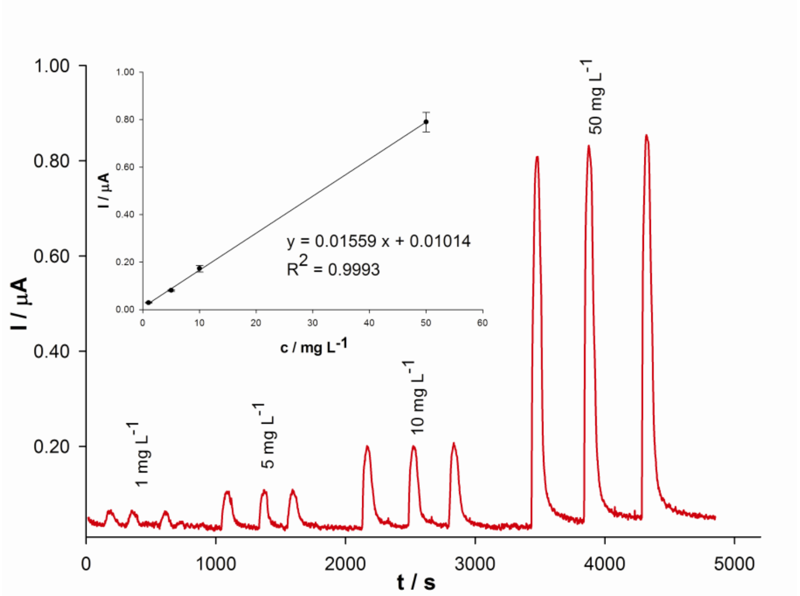


Figure 10. Calibration curve for different concentrations (from 1 to 50 mg L^{-1}) of CySH. Electrode Na[RuCl$_2$L$_2$]/MWCNT/Nafion/SPCE, operating potential +0.15 V *vs.* Ag/AgCl, BR buffer (pH 5.50), flow rate 0.40 mL min^{-1}, injection volume 250 μL

3.6. Real sample analysis

The proposed FIA procedure with Na[RuCl$_2$L$_2$]/MWCNT/Nafion modified screen printed carbon sensor was applied for determination of *L*-Cysteine in pharmaceutical products. Quantitative determinations were carried out by injecting sample solutions into the FIA-system (Fig. 11). Analysis results of the CySH in capsules are given in Table 1.

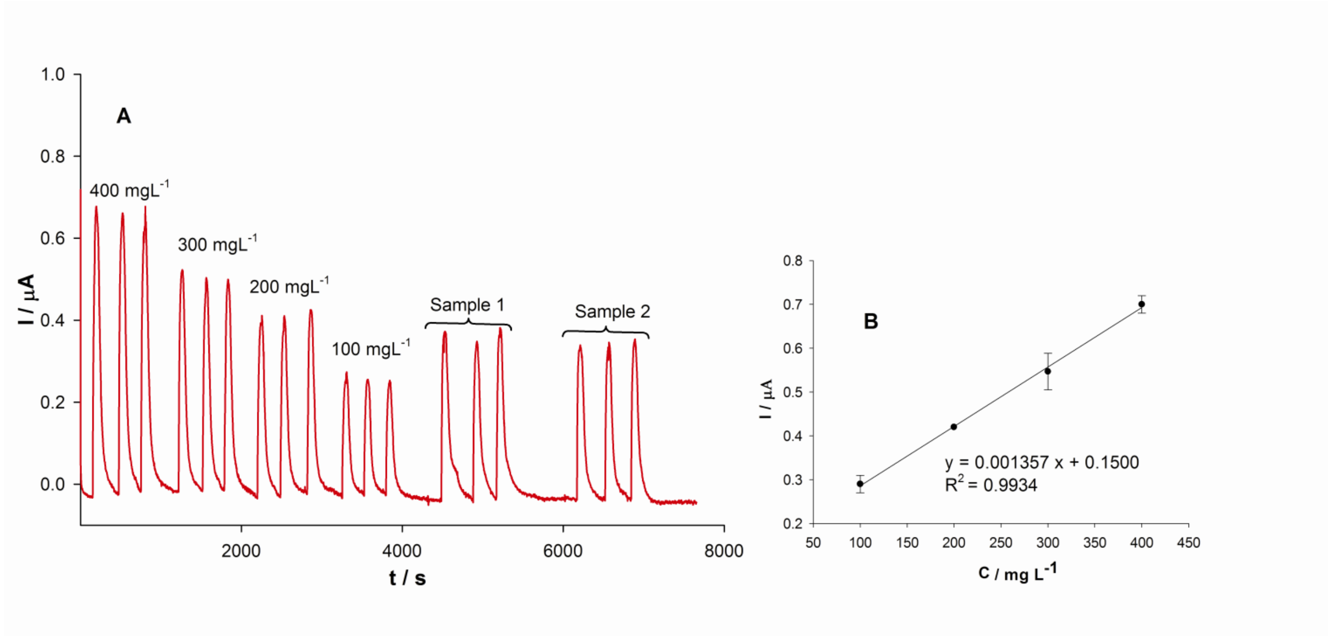


Figure 11. (A) Amperometric FI response of CySH at Na[$RuCl_2L_2$]/MWCNT/Nafion/SPCE, operating potential +0.15 V *vs*. Ag/AgCl, BR buffer (pH 5.50), flow rate 0.40 mL min^{-1}, injection volume 100 μL. (B) Calibration curve for various concentrations of CySH (100 - 400 mg L^{-1}) at Na[$RuCl_2L_2$]/MWCNT/Nafion/SPCE

Table 1. Determination results of CySH in a pharmaceutical products using FIA (n=3)

Method	**Sample**	**Added CySH (mg L^{-1})**	**Found CySH (mg L^{-1})**	**Recovery(%)**
FIA	1	200	195	97.50
	2	200	190	95.00

Table 2. Comparison of the proposed sensor for determination CySH with others

Electrode	**Modifiers**	**Method**	**Limit of Detection (mg L^{-1})**	**Linearity Range (mg L^{-1})**	**Ref.**
CPE[a]	Titanium Phosphate modified with silver hexacyanoferrate	Voltammetric	40.46	24.23 – 1090.4	[36]
GCE	Graphene nanosheets/manganese oxide nanoparticles	Amperometric	0.0091	0.12 – 14.54	[37]
CFE[b]	Micro Au	Voltammetric	0.06	0.5 – 5	[12]
CCE[c]	[Ru(tpy)(bpy)Cl]PF_6	Amperometric	0.12	0.6 – 84.81	[22]
CPE	Y_2O_3 nanoparticles/nitrogen-doped reduced graphene oxide	Amperometric	0.10	0.16 – 87.24	[38]
GCE	Iron tetrasulfonated phthalocyanine/MWCNTs	Amperometric	0.13	1.21 – 24.23	[39]
SPCE	Na[$RuCl_2L_2$]/MWCNT/Nafion	Amperometric	0.11	50 – 500	This work

[a] Carbon paste electrode; [b] Carbon fiber electrodes; [c] Carbon ceramic electrode

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

4. CONCLUSIONS

This work demonstrates the use of carbon sensor, based on glassy carbon and screen printed electrodes, modified with MWCNTs and Ru(III) Schiff base complex, for the determination of CySH. The study presented here shows that MWCNTs and $Na[RuCl_2L_2]$ in combination with Nafion, may improve the voltammetric and amperometric behavior of CySH at the above-mentioned carbon electrodes. From the point of view of sample analysis, FIA seems preferential over voltammetry. It has been shown that SPCE electrodes modified with MWCNTs and $Na[RuCl_2L_2]$ can be useful sensors for quick determination of CySH, as demonstrated with a pharmaceutical samples of CySH.

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