Electrochemical Oxidation of 2,5-Dimercapto-1,3,4-thiadiazole on Carbon Electrodes Modified with Ru(III) Schiff Base Complex

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Abstract
The thiol compound 2,5-dimercapto-1,3,4-thiadiazole is a potential cathode material. The redox reactions of the mentioned thiol compound are slow at room temperature but can be enhanced using electron transfer mediators. The electrochemical oxidation of 2,5-dimercapto-1,3,4-thiadiazole on the surface of carbon electrodes modified with Ruthenium(III) Schiff base complex was studied by voltammetric methods and amperometric flow injection analysis. The electrocatalytic properties of Ruthenium(III) Schiff base complex on glassy carbon and screen printed carbon electrodes are enhanced by the addition of multi-walled carbon nanotubes and Nafion. Voltammetric studies showed that anodic oxidation of DMcT on a modified glassy carbon electrode occurs at a potential of +0.28 V vs. Ag/AgCl in Britton-Robinson buffer (pH 6.50). Flow injection amperometric measurements were performed at +0.20 V vs. Ag/AgCl in Britton-Robinson buffer solutions pH 6.50 at a 0.40 cm$^3$ min$^{-1}$ flow rate. The results of amperometric measurements for modified screen printed and glassy carbon electrodes showed that the screen printed electrode had a lower value of detection limit (0.38 mg dm$^{-3}$) and quantification (1.28 mg dm$^{-3}$) than a linear dynamic range from 1 to 500 mg dm$^{-3}$ of 2,5-dimercapto-1,3,4-thiadiazole. Modified glassy carbon electrode provided a linear dynamic range up to 750 mg dm$^{-3}$ of 2,5-dimercapto-1,3,4-thiadiazole with a detection limit of 3.90 mg dm$^{-3}$ and quantification of 13.20 mg dm$^{-3}$.

Keywords
2,5-dimercapto-1,3,4-thiadiazole, Ru(III) Schiff base complex, carbon electrodes, multi-walled carbon nanotubes, voltammetry and amperometric analysis

1 Introduction
The thiol compound 2,5-dimercapto-1,3,4-thiadiazole (DMcT) has been the most studied thiol compound in the last decade as a potential cathode material due to its high theoretical capacity.1 Except as a cathode material, DMcT is also used as a corrosion inhibitor,2-3 biocide,4 as an intermediate or starting material for pharmaceuticals and dyes, and metal chelating agent.5,6

Due to its wide range of uses, it is important to study its oxidation and detection. There is a need to develop sensitive, simple, fast, and easily accessible methods for determining DMcT. The most commonly used analytical techniques for the determination and quantification of DMcT are capillary zone electrophoresis (CZE) and high performance liquid chromatography (HPLC) with UV detection.7,8 These methods require expensive and non-portable instrumentation, trained personnel, sophisticated sample preparation, and suffer from numerous chemical interferences. The electrochemical techniques have some advantages like simplicity, fast response, wide linear dynamic range, ease of miniaturization, high sensitivity and low cost compared to other methods.9

The oxidation of thiol compounds at the solid electrodes (such as Au, Pt, carbon and graphite), at room temperature, is very slow and requires a potential of at least +1.00 V.10 Therefore, finding appropriate electron transfer mediators for low potential and fast determination of DMcT is of great importance. Organic compound poly(3,4-ethylenedioxythiophene) has been used as a mediator for DMcT oxidation at different electrodes.11,12

Ru complexes have been the subject of numerous studies because of their catalytic, anti-tumour, and electron transfer mediator activity.13,14 Ruthenium(III) complexes were studied as chemical modifiers for carbon electrodes due to their electrochemical behaviour, they are efficient mediators and catalyse reactions of organic substances. To solve problems with overpotential for the quantification of L-cysteine and ascorbic acid with carbon electrodes, in our previous research we studied electron transfer mediator properties of Ru(III) complex compound.15,16 Immobilized on the surface of the carbon electrode, the Ru complexes transfer electrons between the analyte solution and the electrode substrate, resulting in a decrease in activation overpotential.

This work demonstrates the electrochemical behaviour of DMcT on carbon electrodes modified with water-insoluble mediator sodium dichlorobis(N-phenyl-5-bromosalicylideneiminato-N,O)ruthenat(III) complex, hereinafter referred to as Na[RuCl$_2$(SB)$_2$] (Fig. 1), multi-walled carbon nano-
2 Experimental

2.1 Reagents and solutions

Ru(III) Schiff base anionic complex of the general formula Na[RuCl$_2$(SB)$_2$] was synthesized according to the published procedure. The 5 % Nafion solution in a mixture of lower aliphatic alcohols and water was purchased from Sigma-Aldrich (USA). A 1 % Nafion solution was prepared by diluting a 5 % solution with ethanol. High purity (>95 %) MWCNTs were used to improve mediating properties of the Ru(III) Schiff base complex. MWCNTs were purchased from Nanolab (Waltham, MA). The Britton-Robinson buffer solution (BR buffer solution) was prepared by mixing the appropriate volumes of previous solutions that were injected was 100 mmol dm$^{-3}$ acetic acid, 0.040 mmol dm$^{-3}$ boric acid, and 0.040 mol dm$^{-3}$ phosphoric acid. The pH of the resulting solution was adjusted with 0.20 mol dm$^{-3}$ NaOH. A solution of phosphate buffer (0.10 mol dm$^{-3}$) was prepared by mixing the appropriate volumes of previously prepared aqueous solutions of NaH$_2$PO$_4$·2H$_2$O and Na$_2$HPO$_4$·2H$_2$O. Buffer solutions were sonicated under reduced pressure to remove dissolved gases, and then degassed with the argon flow (99.995 %, Messer, Austria). Doubly distilled water was used to prepare all solutions.

Working solutions of DMcT were prepared before measurements by diluting the stock solution of DMcT with a suitable buffer solution. The 2,5-dimercapto-1,3,4-thiadiazole, and others used chemicals were purchased from Sigma Aldrich (USA) as analytically pure.

2.2 Methods and electrode preparation

Voltammetric and amperometric measurements were performed using an Autolab Potentiostat /Galvanostat (PG-STAT 12) coupled to PC. The Autolab software GPS Version 4.8 was used to control the instrument. The working electrodes were a bare and modified glassy carbon electrode (GC electrode, Metrohm, 0.28 cm$^2$ surface area), and a screen printed carbon electrode (SPC electrode, Coors Ceramic GmbH, USA, 35 × 4 mm). All obtained potentials are given versus the Ag/AgCl reference electrode at room temperature. Cyclic voltammograms (n = 3) of DMcT were recorded in the potential range between −0.25 V and +0.35 V (scan rate of 100 mV s$^{-1}$) in BR buffer solutions pH 6.50, using bare and modified GC electrodes as working electrode, Ag/AgCl electrode (Metrohm 6.0733.100 LL) as a reference, and a platinum wire as a counter electrode. Differential pulse voltammograms of DMcT were recorded in potential range from 0.00 to +0.60 V applying scan rate of 20 mV s$^{-1}$ in BR buffer solutions pH 6.50, a pulse time of 0.05 s, pulse amplitude +0.025 V, using bare and modified GC electrodes as working, a platinum wire as counter, and Ag/AgCl as a reference electrode. Square wave voltammetry was measured in the potential range from 0 to +0.40 V, pulse interval 5 s, frequency 25 Hz, scan rate 40 mV s$^{-1}$ in BR buffer solutions pH 6.50, amplitude +0.020 V, SWV measurements as well as other voltammetric measurements were performed in a cell with a volume of 5 cm$^3$. Amperometric measurement was carried out using flow injection system that involved of a high performance liquid chromatographic 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 and MF-1048, BAS) were used to adjust the thickness of the flow-through cell. The amperometric measurement of DMcT was achieved by measuring the current response at a constant potential (+0.20 V). The flow rate of the BR buffer solution was 0.40 cm$^3$ min$^{-1}$, using modified GC and SPC as working electrodes, Ag/AgCl (3 mol dm$^{-3}$ KCl, BAS RE-1) as reference, and backplate of the flow cell as a counter electrode. The volume of DMcT solution that was injected was 100 µL. The carbon electrodes were modified with the Na[RuCl$_2$(SB)$_2$], MWCNTs, and Nafion solution according to a procedure of Pazalja et al. The electrodes modification procedure is shown in Fig. 2.

3 Results and discussion

3.1 Voltammetry studies

Cyclic, differential pulse, and square wave voltammetry were used to demonstrate the mediating properties of Na[RuCl$_2$(SB)$_2$] and the oxidation of DMcT at the modified GC electrodes. Cyclic voltammograms were obtained with unmodified and modified GC electrode in the potential range between −0.25 V and +0.35 V at a scan rate of 100 mV s$^{-1}$. Cyclic voltammograms of DMcT at unmodified GC electrode are shown in Fig. 3A. The unmodified electrode displays no redox peaks in the investigated potential range because the oxidation process of thiol compounds, including DMcT, is a slow process on the surface carbon electrodes that require high values of positive potentials. Fig. 3B represents the cyclic voltammograms of electrochemical oxidation of DMcT on a modified GC...
At the electrode modified with Ru(III) Schiff base complex, the anodic well-defined peak of DMcT oxidation evident at +0.28 V (Fig. 3B-curve a) indicates excellent mediating properties of Na[RuCl₂(SB)₂]. After the addition of MWCNTs and Nafion to the modification mixture, the oxidation peak is more intense (∆I = 12.80 µA) and appears at potential +0.29 V (Fig. 3B-curve b). Since Nafion has a strong capacity to dissolve MWCNTs and Na[RuCl₂(SB)₂], it has been used for dissolving and binding of those substances to the surface of carbon electrodes during the electrochemical measurement.\(^{15,21}\) The cathode peak was not observed during the reverse scan at the investigated potential range (−0.25 to +0.35 V) because oxidation of thiol compounds is an electrochemically irreversible process.\(^{22,23}\) The results show that, compared to the unmodified GC electrode, the mediating role of Na[RuCl₂(SB)₂] and the conductive properties of MWCNTs result in a decreased value of the potential required for DMcT...
Squissato et al. introduced oxidation of DMcT at bare disposable screen printed graphite electrodes at the potential of +1.30 V, which is a significantly higher value related to the potential of +0.28 V. The mechanism of oxidation of DMcT involves the transfer of two electrons and two protons forming a disulphide dimer in the acidic medium. Similar to those for other thiol compounds, the oxidation process of DMcT on the surface of solid electrodes forms thiyl radical (reaction 1), which further dimerizes to disulphide (reaction 2).

\[ R - SH \rightarrow R - S_{sh}^* + H^+ + e^- \quad (1) \]
\[ 2R - S_{sh}^* \rightarrow R - SS - R \quad (2) \]

Since Naion has a strong capacity to dissolve MWCNTs and Na[RuCl₂(SB)₂], it has been used for dissolving and binding of those substances to the surface of carbon electrodes during the electrochemical measurement. The mediating properties of the Ru(III)/Ru(II) pair for the oxidation of DMcT on the glassy carbon electrode were demonstrated also using differential pulse voltammetry and square wave voltammetry. The well-defined anodic peak obtained using a modified GC electrode at +0.28 V corresponding to DMcT oxidation, clearly indicates excellent mediating properties of Na[RuCl₂(SB)₂] (Fig. 4).

Furthermore, square wave voltammetry was used to investigate electrochemical oxidation of DMcT at a modified GC electrode. As shown in Fig. 5A, an increase in DMcT concentration causes an increase of anodic peak current (+0.28 V), suggesting a good electrochemical response of the modified electrode. Fig. 5B shows the dependence of the DMcT concentration versus anodic current response. The modified electrode demonstrates a linear dependence, with correlation factor \( R^2 = 0.9882 \).

At the surface of the Na[RuCl₂(SB)₂]/MWCNTs/Nafion GC electrode, the DMcT is oxidised to 5,5'-disulfanediyldibis (1,3,4-thiadiazol-2-amine), while the Ru(III) is reduced to a Ru(II) complex compound. The resulting Ru(II) complex is electrochemically re-oxidised to the Ru(III) complex, producing an oxidation current proportional to the DMcT concentration (Fig. 2). The oxidation of DMcT at the Na[RuCl₂(SB)₂]/MWCNTs/Nafion GC electrode was recorded at a potential of +0.28 V for all three voltammetric methods. The potential of +0.28 V is a significantly lower value than those reported in the literature.
3.2 Amperometric study

3.2.1 Optimisation of working conditions

Since Na[RuCl$_2$(SB)$_2$] and MWCNTs showed remarkable mediating properties in DMcT oxidation, the operating parameters for the analytical determination of DMcT were optimised using flow injection amperometry. Fig. 6A shows the dependence of the (a) background current, and (b) amperometric response for 200 mg dm$^{-3}$ DMcT at an applied potential from $-0.20$ V to $+0.40$ V in BR buffer solution (pH = 6.50), and flow rate 0.40 cm$^3$ min$^{-1}$ for Na[RuCl$_2$(SB)$_2$]/MWCNTs/Nafion SPC electrode. For negative potential values, the DMcT current response has low values, as well as an unstable background current. Increasing the potential value also increases the current response. However, high values of positive potentials are not recommended and electrodes are modified with mediators to prevent overpotential of the analyte. The previously reported results showed that the oxidation of DMcT takes place at positive values of the potential and its reduction at negative ones, which is in accordance with the results of this study.$^{30}$ At a potential of $-0.20$ V to 0 V, no anode peaks were observed. Working potential of $+0.20$ V was selected for subsequent amperometric detection in the FIA experiments because: (i) the background current was stable and had values near to zero, (ii) it was low enough to reduce any interferences, (iii) the amperometric response was satisfactory and very reproducible.

The electrochemical behaviour of DMcT was studied in phosphate and BR buffer solution in the pH range from 3.50 to 9 (Fig. 6B). The amperometric response of oxidation DMcT on the modified GC electrode was found to have a higher value in BR buffer compared to phosphate buffer. The highest value of the current was obtained at a pH value of 6.50. Therefore, all further measurements were performed in BR buffer at a pH value of 6.50. Next, the flow rate was evaluated in order to obtain the highest signal for DMcT oxidation. Fig. 7 shows the dependence of the FIA signal on the flow rate of the BR buffer solution for 200 mg dm$^{-3}$ DMcT. The current response displays an inverse relationship with the flow rate, the higher the flow rate the lower the current response. The flow rate of 0.40 cm$^3$ min$^{-1}$ was selected for subsequent experiments because it reduces the time consumed on analyses and the current response is satisfactory.

![Graph](image1)

**Fig. 6** – Dependence of the FI amperometric response of DMcT at Na[RuCl$_2$(SB)$_2$]/MWCNTs/Nafion SPC electrode on the: (A) applied potentials (a-background current, b-current response for 200 mg dm$^{-3}$ of DMcT); (B) applied pH in BR and phosphate buffer solutions (0.10 mg dm$^{-3}$)

**Slika 6** – Ovisnost FI amperometrijskog odziva DMcT-a na Na[RuCl$_2$(SB)$_2$]/MWCNT/Nafion SPC elektrodi o: (A) primijenjenom potencijalu (a-osnovna struja; strujni odziv za 200 mg dm$^{-3}$ DMcT-a); (B) pH vrijednosti za otopine BR i fosfatnog pufera (0.10 mg dm$^{-3}$)

![Graph](image2)

**Fig. 7** – Dependence of the FIA peak current response of DMcT (200 mg dm$^{-3}$) at Na[RuCl$_2$(SB)$_2$]/MWCNT/SPC electrode on the flow rate of the carrier

**Slika 7** – Ovisnost FIA strujnog odziva DMcT-a (200 mg dm$^{-3}$) na Na[RuCl$_2$(SB)$_2$]/MWCNT/SPC elektrodi o brzini protoka nosača
3.2.2 Calibration curves, detection and quantification limits

Linearity, the limit of detection and quantification were investigated for three Na[RuCl₃(SB)₂]/MWCNT/Nafion/GC modified carbon electrodes. One GC electrode and two SPC electrodes with and without MWCNTs addition. The amperogram for the modified GC electrode is shown in Fig. 8. For the same electrode, the linear relation between the amperometric peak current and different concentrations of DMcT was tested by injecting (n = 3) standard solutions into the FIA system under optimal parameters. The experiments revealed a good linear response for DMcT concentrations ranging from 5 to 750 mg dm⁻³, as shown in Fig. 9B, in agreement with the following equation:

i(μA) = 0.0114 [DMcT] (mg dm⁻³) + 0.0570, \( R^2 = 0.9949 \).

The limit of detection (LOD) obtained for Na[RuCl₃(SB)₂]/MWCNT/Nafion/GC electrode was 3.90 mg dm⁻³ (3σ/slope method). Furthermore, the quantification limit (LOQ) of 13.20 mg dm⁻³ was determined by 10σ/slope. The repeatability was found as 2.10 %.

After amperometric studies of DMcT oxidation at the modified GC electrode, measurements were also performed for the SPC electrodes. Figs. 10A and 11A show typical amperograms for different concentrations of DMcT using Na[RuCl₃(SB)₂]/Nafion/SPC and Na[RuCl₃(SB)₂]/MWCNT/Nafion/SPC electrodes as detectors, respectively. The obtained results for Na[RuCl₃(SB)₂]/Nafion/SPC electrode showed a good linear response for DMcT concentrations from 5 to 100 mg dm⁻³, as demonstrated in Fig. 10B: i(μA) = 2.2415 \times 10^{-3} [DMcT] (mg dm⁻³) + 1.7568 \times 10^{-3}, \( R^2 = 0.9919 \).

The limit of detection (LOD) obtained for Na[RuCl₃(SB)₂]/Nafion/SPC electrode was 1.55 mg dm⁻³. LOQ was calculated as 5.17 mg dm⁻³. Between 10 replicate injections of DMcT, the repeatability was found to be 2.40 %.

Obtained results using Na[RuCl₃(SB)₂]/MWCNTs/Nafion/SPC electrode as detector showed linear relation between the amperometric peak current and concentration of DMcT in the concentration interval from 1 to 100 mg dm⁻³ in a BR buffer solution (pH 6.50): i(μA) = 0.0274 [DMcT] (mg dm⁻³) + 0.0563, \( R^2 = 0.9970 \) (Fig. 11B). LODs were calculated as 0.38 mg dm⁻³ and LOQ as 1.28 mg dm⁻³. The repeatability was found as 1.80 % (n = 10).

Since MWCNT has excellent catalytic effects due to high surface activity and electronic conductivity, amperomet-
ric current response of the SPC electrode modified with Na[RuCl$_2$(SB)$_2$] and MWCNTs is significantly higher than the SPC electrode modified with the mixture without MWCNTs. Furthermore, for an MWCNTs-modified electrode, the lowest detectable concentration value is 1 mg dm$^{-3}$, whereas, for an unmodified electrode it is 5 mg dm$^{-3}$. The widest linearity was achieved at the GC electrode modified with Ru(III) complex and MWCNTs (Fig. 9). Additionally, the lowest detection limit, among the used electrodes, was obtained at the SPC electrode modified with Ru(III) Schiff base complex and MWCNTs. That indicates that the addition of MWCNTs improves the mediating properties of Na[RuCl$_2$(SB)$_2$] for DMcT oxidation at carbon electrodes.

4 Conclusion
Thiol compound 2,5-dimercapto-1,3,4-thiadiazole is oxidized at high potentials at the surface of carbon electrodes. Voltammetric measurements demonstrated that the combination of the catalytic properties of sodium dichlorobis[N-phenyl-5-bromosalicylideneiminato-N,O] ruthenat(III) complex with MWCNTs and Nafion provided electrochemical oxidation at much lower positive potentials compared to unmodified carbon electrodes. It has been shown that, under optimal conditions, SPC electrodes modified with Ru(III) complex, MWCNTs and Nafion can be useful sensors and enable low-potential amperometric measurements of DMcT. The modified SPC electrode...
demonstrated better sensitivity (LOD = 1.55 mg dm⁻³⁻¹), while a wide linear range was obtained by the GC electrode (5–750 mg dm⁻³⁻¹). In conclusion, findings from the present study emphasize the application of these modified electrodes for the determination of DMcT in real samples.

List of abbreviations

Popis kratica

| Abbreviation | Description |
|--------------|-------------|
| DMcT         | 2,5-dimercapto-1,3,4-thiadiazole |
| CZE          | capillary zone electrophoresis |
| HPLC         | high performance liquid chromatography |
| UV           | ultraviolet |
| SPC          | screen printed carbon |
| FIA          | flow injection analysis |
| LOD          | limit of detection |
| LOQ          | limit of quantification |

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SAŽETAK
Elektrokemijska oksidacija 2,5-dimerkapto-1,3,4-tiadiazola na ugljikovim elektrodama modificiranim s Ru(III) kompleksom sa Schiffovim bazama
Mirna Pazalja

2,5-dimerkapto-1,3,4-tiadiazol (DMcT) je tiolni spoj i potencijalni katodni materijal. Redoks-reakcije navedenog tiolnog spoja sporao se odvijaju pri sobnoj temperaturi, ali se mogu ubrati upotrebom medijatora za prijenos elektrona. Elektrokemijska oksidacija DMcT na površini ugljikovih elektroda modificiranih rutenijskim kompleksom sa Schiffovim bazama, ispitana je voltametrijskim metodama i amperometrijskom analizom s injektiranjem u protok. Elektrokatalitička svojstva rutenijskom kompleksa sa Schiffovim bazama na elektrodii od staklastog ugljika i printanoj ugljikovoj elektrodi poboljšane su dodavanjem višeslojnih ugljikovih nanocjevčica i Nafiona. Voltametrijska ispitivanja pokazala su da se anodna oksidacija DMcT na modificiranoj elektrodi od staklastog ugljika odvija na potencijalu od +0,28 V u odnosu na Ag/AgCl u Britton-Robinsonovom puferu (pH 6,50). Amperometrijska mjerenja provedena su na +0,20 V u odnosu na Ag/AgCl u Britton-Robinsonovom puferu pH 6,50 pri brzini protoka od 0,40 cm³ min⁻¹. Rezultati amperometrijskih mjerenja, za modificiranu elektrodu od staklastog ugljika i printanu ugljikovu elektrodu, pokazali su da printana ugljikova elektroda ima nižu vrijednost granice detekcije (0,38 mg dm⁻³) i kvantifikacije (1,28 mg dm⁻³) te linearni dinamički raspon od 1 do 500 mg dm⁻³ DMcT. Modificirana elektroda od staklastog ugljika pokazala je linearni dinamički raspon do 750 mg dm⁻³ DMcT, granicu detekcije 3,90 mg dm⁻³ i kvantifikacije 13,20 mg dm⁻³.

Ključne riječi
2,5-dimerkapto-1,3,4-tiadiazol, rutenijskom kompleks sa Schiffovim bazama, ugljikove elektrode, višeslojne ugljikovе nanocjevčice, voltametrija i amperometrijska analiza