CHEMICALLY MODIFIED ELECTRODE FOR NO_2^- DETERMINATION IN ENVIRONMENTAL APPLICATIONS

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În această lucrare se obţine un electrod modificat chimic cu o porfirină de cobalt bipiridil tetrarutenata Co(III)TPy{Ru(II)(dipy)(L)Cl}₄](TFMS), selectiv pentru anionul nitrit şi se prezintă o aplicaţie a acestui electrod în determinări de nitrit din ape minerale efectuate în celule standard şi de analiză flow-injection.

The work presents the preparation of Co(III) bipyridil tetraruthenated porphyrin Co(III)TPy{Ru(II)(dipy)(L)Cl}₄](TFMS) chemically modified electrode selective for nitrite and an application for the determination of nitrite ion in mineral water performed in standard and flow injection analysis cells.

Keywords: Co(III) bipyridil tetraruthenated porphyrin Co(III)TPy{Ru(II)(dipy)(L)Cl}₄](TFMS), chemically modified electrodes, nitrite determination, flow injection analysis

1. Introduction

In order to widen the application field of electroanalytical methods it is important to develop novel electrode systems with specific responses in real samples. The bioavailability and toxicity of many pollutants is related to the chemical species found in the environment in which the element is present.

Sensors are classified according to several criteria [1], considering the transducing mechanism, recognition principle or applications. Nanoelectrodes are new electrochemical tools that can find applications in electroanalytical sensing for trace and ultra trace concentration levels in environmental samples [2-5].

Nitrite is widely used as preservative and fertilizing agent. A continuous exposition to these pollutant can induce severe health implications. Nitrite can react irreversibly with hemoglobin reducing thus, blood ability for oxygen transport. Due to its possible carcinogenic effects the nitrite detection in

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environment plays an important role. A large number of analytical methodologies are based on electrochemical, chromatographic and spectrophotometric techniques. The electrochemical methods offer useful alternatives [6-7]. Electrochemical techniques allow preparation and testing of sensitive and selective chemically modified electrodes (CMEs) for NO_2^- determination. The electrocatalytic property is one of the distinguishable features of CMEs to be utilized in this purpose. In Fig. 1, several preparation routes for CMEs are presented.
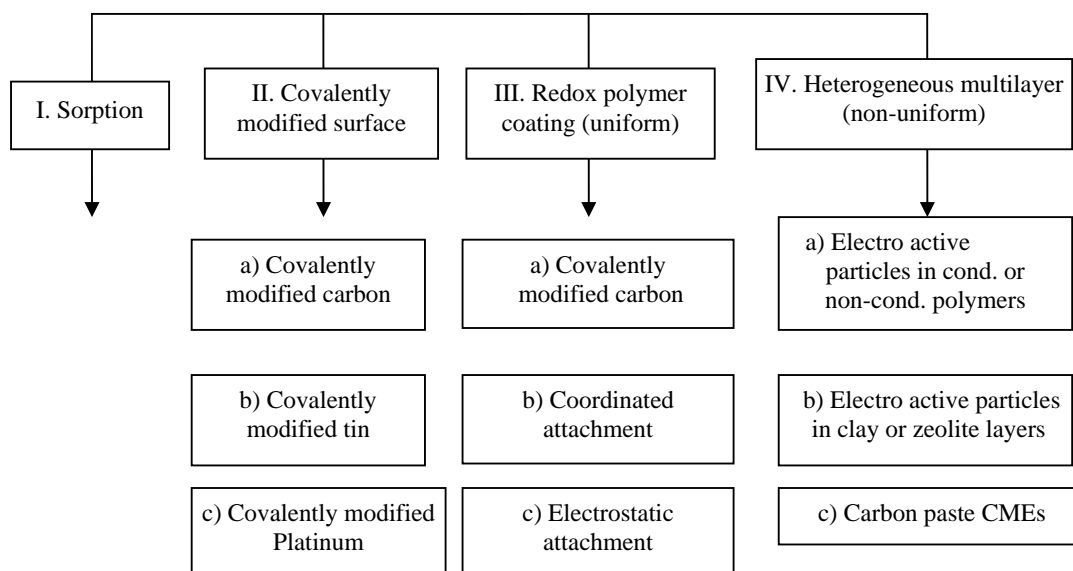

Fig.1. Schematic representation for various kinds of CME preparation routes

Another possibility to form uniform multi-component films, which contain redox-functionalized ligands is by utilization of electrochemical co-deposition technique [8].

The ligands based on Co (III) bipyridil tetraruthenated porphyrins form homogeneous films by adsorption or electropolymerization. Such films exhibit electrical response allowing applications as amperometric sensors. Co(III)TPy{Ru(II)(dipy)(L)Cl}4](TFMS) is a metalloporphyrin of great interest in designing CME, its electrocatalytic properties being already investigated by immobilizing molecular materials on solid electrode surfaces, these being deposited as electrochemically active films generated by dip-coating, electrostatic assembly or electro polymerization methods [9-10]. The present work investigates the electrochemical behaviour of Co(III)TPy{Ru(II)(dipy)(L)Cl}4](TFMS) having the following structure:
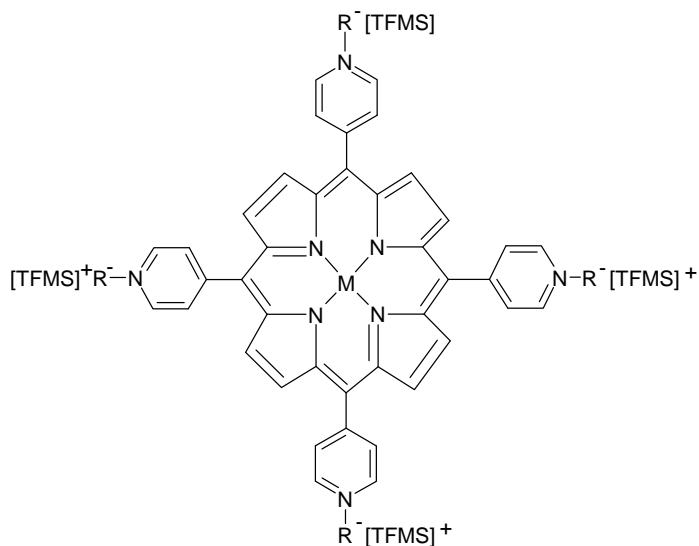
Fig.2. Structure of [Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS), where R is [Ru(bipy)LCl]$^+$ and TFMS$^-$ represents trifluoromethanesulfonate ion.

The Co(III) bipyridil tetraruthenated porphyrin, Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) is a large molecule which undergoes multiple electrochemical processes due to the big number of electro active centres. The Ru(II) complexes with 2.2'-dipyridil can be oxidized to Ru(III) complexes each ligand being successively reduced. The porphyrin ring can be oxidized or reduced to radical cation and the corresponding dication or to the radical anion and the corresponding dianion. The central metallic ion is electrochemically active, too. It is known that starting from -0.2 V in anodic direction, it appears a reversible couple at E$_{1/2}$ = 0.93 V [3]. This wave corresponds to a weak interaction between the four ruthenated substituents. At 0.8 V it could be observed a weak adsorption pre peak. Voltammetric studies at potentials higher than 1 V in DMF indicate the presence of important residual currents.

2. Experimental

Reagents. Acetonitrile (CH$_3$CN, Rathburn, HPLC grade) was used as received and stored under an argon atmosphere. Tetra-n-butylmmonium perchlorate (TBAP, Fluka) was re-crystallized from ethyl acetate + cyclohexane and dried under vacuum at 80°C for three days. Tetraethyl ammonium hexafluoro phosphate (TEAPF$_6$) was used as received. The synthesis of Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) was previously described [].

Apparatus. All electrochemical measurements were performed using an Autolab with PGSTAT 30, at which a standard and a flow injection analysis (FIA) cells were coupled.

Procedure. The electrochemical characterization of Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) in CH$_3$CN, the polymerization and the characterization of the resulting modified electrodes were run at room temperature under an argon atmosphere using a conventional three-electrode electrochemical cell. An Ag/10 mM Ag$^+$ in CH$_3$CN + 0.1 M TBAP electrolyte was used as the reference electrode. The working electrodes were platinum disks (5 mm diameter) systematically polished with 1 μM diamond paste, cleaned with a Transsonic T 460 sonication apparatus and successively washed with water and ethanol.

3. Results and discussion

3.1. Electrochemical study of the ligand

Among numerous cobalt porphyrins, electrochemical studies in non aqueous media were mainly focused on Co based on the conventional complexing macrocycle Co(III) bipyridil tetraruthenated porphyrin. The reversible pair of waves at 0.93 V (Fig. 3) assigned to the Ru(III/II) process is not sensitive to the coordination of Co(II) ion. The anodic peaks found around 1.3 to 1.6 V in a typical EC mechanism behaviour were assigned to the oxidation of porphyrin ring to the radical cation or dication.
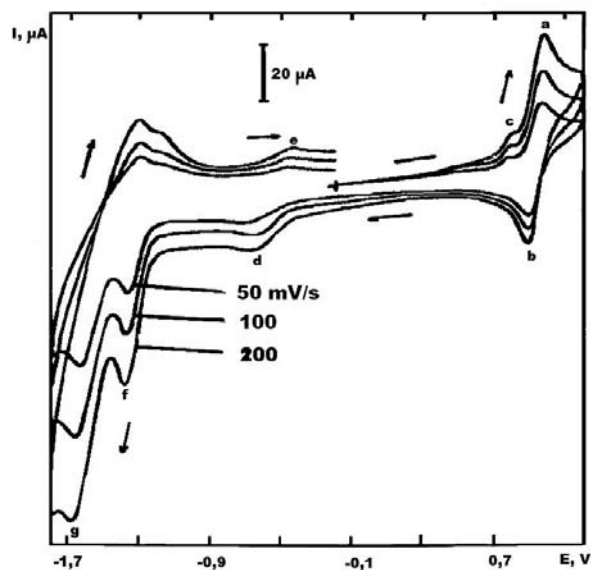
Fig. 3. Cyclic voltammograms of 1 mM [Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) in DMF containing 0.1 M TEAPF$_6$ on Pt disk working electrode, Ag/Ag$^+$ (0.010 mol.dm^{-3} in CH$_3$CN) reference electrode and a coiled platinum wire auxiliary electrode were employed.

In Fig. 3, it can be seen that in the scan from -0.2 V in anodic direction a reversible couple (a/b) at E$_{1/2}$ = 0.93 V appears. This wave corresponds to a weak interaction between the four ruthenated substituents, at 0.8 V being observed a weak adsorption pre-peak (c). Scanning the potential in cathodic direction gives birth to a weak reduction wave at approx. -0.5 V (d), associated to Co-porphyrin complex, followed by two intense reduction waves at E = -1.37 V(f) and -1.63 V (g). The   peak (f) is assigned to the bipyridine ligand from each ruthenated substituent. The more negative wave (g) has approximately the same intensity with wave (f), its potential being similar to that found in reducing the second bipyridine ligand from ruthenated bipyridine complex. This reaction is irreversible, the anodic corresponding wave having small intensities, indicating that the most important part of the reduced species appear in a coupled chemical reaction. The Co(III)/Co(II) waves do not appear in the voltammogram due to the slow kinetic of the electron transfer process in the Co(III) complexes on the electrode. This wave is usually observed in the absence of strong coordinated ligands.

3.2. Preparation of CME

The complex was dissolved in tetra-n-butylmmonium perchlorate 0.1 M in acetonitrile. The film growth is realized through repeated scans between - 0.4 and + 1.2 V (Fig. 4). A constant growth of the current electroactivity could be attributed to the increase of the amount of Ru(II)/(III) couple in the polymeric film. A very thin, adherent film could be seen on the electrode surface. Co(III) complex gives films having good homogeneity, stability and adherence. The films are not soluble in water, their dissolution being prevented by the presence of the contra ion TFMS⁻. In aqueous solutions, cyclic voltammograms of the chemically modified electrodes have one pair of well-defined waves with E^{pc} = 0.93 V and E^{pa} = 0.98 V assigned to redox couple Ru(III)/(II). The anodic and cathodic waves are well-defined and the current is proportional with the scan rate. The half-width of the peak is approx. 120 mV, indicating weak repulsions between redox centres. The peak currents are proportional with the amount of complex transferred at the electrode. The coverage degree is approx. 1-2 nmoles/C, showing that ruthenated substituents are electrochemically active.
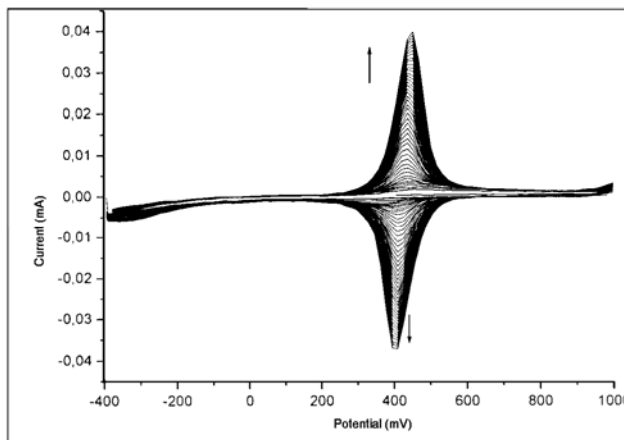

Fig. 4. Voltammogram of the electropolymerization process for a 0.5 mM
[Co(III)TPy{Ru(II)(dipy)(L)Cl}₄]⁵⁺ complex on a 5 mm diameter Pt electrode; 0.1 M TBAP in
acetonitrile; v = 100 mV s⁻¹

3.3. Nitrite recognition

The cyclic voltammograms of the modified electrodes as a function of the concentration of nitrite at pH = 6.8 are shown in Fig. 4. The electrocatalytic wave for the oxidation of nitrite to nitrate occurred at 0.9 V and reached a maximum around 1 V, showing a relatively fast-charge transfer process mediated by a

reversible redox reaction. In addition a significant cathodic shift of the oxidation process appears.
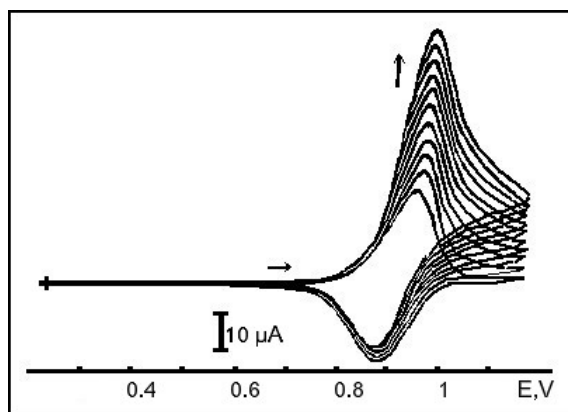

Fig. 5. Cyclic voltammograms of 0 - 1 mM NO$_2^-$ solutions on Co(III) bipyridil tetraruthenated porphyrin CME, $\Gamma = 1.3 \times 10^{-8}$ mol/cm^2 v = 100 mVs^{-1}, acetic acid-acetate buffer (pH=4.7).

4. Application to real samples

This method can be applied to determine nitrite ions in natural waters. Our experiments tested the nitrite ion in commercial mineral water, without any previous treatment.

4.1. NO$_2^-$ determination using CME in standard cell

This method can be applied to determine nitrite ions in standard cell. The result for several nitrite standard additions directly in these water samples are presented in Table 1.
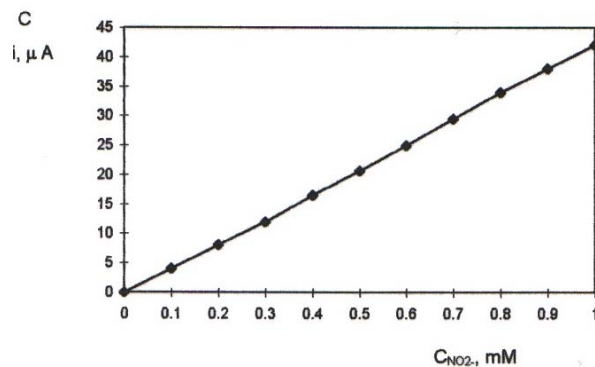

Fig.6. Calibration curve of Co(III) bipyridil tetraruthenated porphyrin CME for NO$_2^-$ determination in mineral water

From Fig. 6 it could be observed a linear response of the electrode in the range 0.1 - 1 mM NO_2^-. This result is in agreement with flow injection analysis, where a better sensitivity of the signal is obtained applying a constant potential to the cell and consecutive injections of NO_2^- solutions, the response being linear in the range 1 - $8x10^{-7}$ M NO_2^-.

Table 1.
Results obtained for nitrite determination in mineral water, in the concentration range from 50 to 700 μM.

Added [NO_2^-] [μM]	Found [NO_2^-] [μM]	Recovery [%]
50.00	49.27	97.9
70.00	65.98	96.4
90.00	93.00	103.2
110.00	113.03	101.9
300.00	292.25	97.3
500.00	497.50	99.4

Table 1 summarizes the results of NO_2^- in water by adding nitrite concentrations in the range from 50 to 500 μM without extra supporting electrolyte. The mean recovery of 98.50 % indicates that the method is applicable to water analysis. By using the standard addition method, linear equation of current (y) vs. NO_2^- concentration (x) is obtained: $y = 0.078x + 0.10$ ($r^2 = 0.9925$).

The electrochemical determination of nitrite is simple, rapid and works without complexation reagents, in contrast to the standard spectrophotometric method, which requires careful control of pH and the use of carcinogenic reagents.

4.2. NO_2^- determination in FIA cells

In flow injection analysis, a better sensitivity is obtained. In this case, a constant potential (E = 1.1 V) is applied to the cell which contains the $Co(III)TPy\{Ru(II)(dipy)(L)Cl\}_4](TFMS)$ chemically modified electrode as indicator electrode. Consecutive injections of NO_2^- solutions with different concentrations are followed as electrochemical currents (Fig. 7).

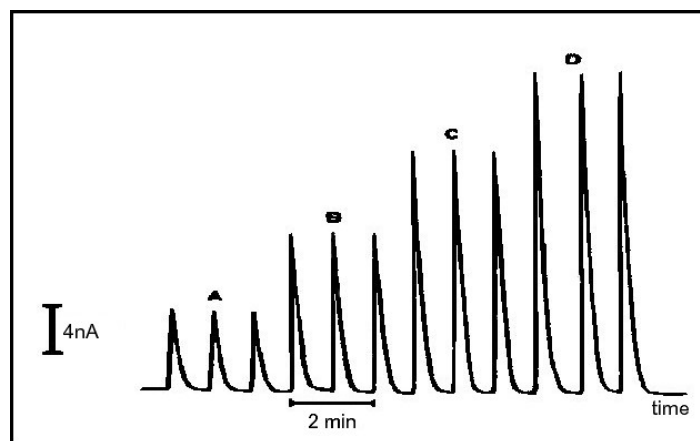Fig.7. The response of the electrode in FIA (flow injection analysis) with NO_2^- CME: (A) $2x10^{-7}$ M, (B) $4x10^{-7}$ M; (C) $6x10^{-7}$ M, (D) $8x10^{-7}$ M, acetic buffer (pH=4.7), $c_{LiTFA}=0.1$ M, flow rate = 0.9 mL/min

5. Conclusions

The CME with Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) porphyrin derivative which reversibly coordinate nitrite ions was characterized. The oxidation of nitrite ions to nitrate occurred at an anodic peak potential of 0.72 V vs. SCE and remained constant and independent of the solution pH over the range between 2.3 and 6.9. Mass transfer and charge transfer control the electrode reaction. The oxidation current is directly proportional to nitrite concentration over a wide range of concentrations. This CME with Co(III)TPy{Ru(II)(dipy)(L)Cl}$_4$](TFMS) proved its potential applications as amperometric sensor in the determination of nitrite ion. A linear response of the electrode in the range 10^{-4} - 10^{-3} M NO_2^- has been observed. By flow injection analysis a better sensitivity of the signal is obtained the response being linear in the range 1 - $8x10^{-7}$ M NO_2^-.

R E F E R E N C E S

[1] *Toma, H. E., Araki, K.*, Coord. Chem. Rev. **2000**, *196*, 307.
[2] *Araki, K., Wagner, M. J., Wrighton, M.S.,* Langmuir **1996**, *12*, 5393.
[3] *Mayer, I, Eberlin, M.E., Tomazela, D.M., Toma, H.E., Araki, K., J. Mex.* Chem. Soc. 2005, **49(2)***,* 180.
[4] *Ugo, P., Moretto L. M., Vezza F.,* Chem.Phys. Chem. 2002, **3**, 917.
[5] *Siemeling, U., Z.* Anorg. Allg. Chem. 2005, **631**, 2957.
[6] *Cosnier, S., Gondran, Ch., Wessel, R., Montforts, F.P., Wede, M.l,* Sensors 2003, **3**, 213.
[7] *Chang, J.,-L., Zen, J. –M*., Electroanalysis 2006,**18(10),** 941.

[8] *Ion, I., Ion, A.C., Barbu, L*., Izvestia Acad.Nauk Respubliki Moldova, Biol. Him. Nauki, 1993, **2**, 61.

[9] *Ion, A.C., Ion, I., Moutet, J.C., Saint-Amman, E., Popescu, A. , Ungureanu, E.M*., Adv. Materials 1997, **9(9***), 71.

[10] *Totir, N., Lupu, S., Ion, A.C., Ion, I.,* Rev. Roum. Chim. 2001, **46(6)**, 3.