Australian Journal of Basic and Applied Sciences, 6(9): 357-363, 2012
ISSN 1991-8178

Electrochemical Interferences of Mn^{2+} with Hg^{2+}, Cd^{2+} and Cu^{2+} at Different Modified GCE

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Abstract: Glassy carbon electrode (GCE) was modified with carbon nanotubes CNT and C_{60} by attachment and solution evaporation techniques, respectively. CNT/Li^+/GCE and C_{60}/Li^+/GCE were prepared by modifying CNT/GCE and C_{60}/GCE in Li^+ solution via cyclic voltammetry (CV) potential cycling. The sensing characteristics of the modified film electrodes, demonstrated in this study for interference of Mn^{2+} in different heavy metals ion esp. Hg^{2+}, Cd^{2+} and Cu^{2+}. The interfering effect was investigated that exert positive interference on the redox peaks of Mn^{2+}. The modification of GCE with nano materials and Li^+ act an enhancement for the redox current peaks to observe the effect of interference for Mn^{2+} in 1:1 ratio with different heavy metals ion.

Key word: cyclic voltammetry-CNT/Li^+/GCE-C_{60}/Li^+/GCE-Mn^{2+}

INTRODUCTION

Many compounds (including heavy metals, HMs) used in different fields of industry and/or agriculture act as inhibitors of enzymes, which, as consequence, are unable to bind the substrate. Even if it is not so sensitive, the method for detecting heavy metal traces using biosensors has a dynamic trend and is largely applied for improving the "life quality", because of biosensor's sensitivity, selectivity, and simplicity (Gazelle and Turdean, 2011; Xueji, *et al,* 2008).

A highly sensitive electrochemical sensor made of a glassy carbon electrode (GCE) coated with a Langmuir–Blodgett film (LB) containing polyaniline (PAn) doped with p-toluenesulfonic acid LB/PAn-PTSA/GCE has been used for the detection of trace concentrations of Ag^+ (Qiongyan *et al*, 2010).

Interferences from other metal ions were investigated of Cd^{2+} could be simultaneously detected in the mixture solution. The proposed method was further applied to the trace levels of Pb^{2+} detection in water samples with satisfactory results (He *et al,* 2010*;* Shenghui and Huang, 2001).

Surface modification by chitosan (CT) on a glassy carbon electrode (GCE) was employed in the present study to determine metal traces (Cu, Pb, Cd, Co, As and Pt). The modified surface exhibited an affinity to chelating metal ions in solution, forming complexes. Cyclic voltammetry technique was used to characterize the polymeric surface behavior in presence of different metals and during the differential pulse voltammetric analysis (Martínez-Huitle *et al*, 2010).

The heavy metals concentrations have been determinate by AA spectrometry and electrochemical methods by cyclic voltammetry and selective ion electrode determinations. The determination of heavy metals concentration in fruits is very important to be known because they both represent a natural and healthy source of vitamins, microelements, mineral salts, sugars, pectin, vegetable fibers necessary to human body equilibrium, and can be "small accumulators" of some toxic metals and their concentration in time can contribute to Alzheimer, hepatic, pancreatic, kidney diseases. The monitoring of heavy metals in fruits represents a possibility to evaluate the degree of medium pollution: soil, water and air (Stefanut *et al,* 2007).

Sensors for electrochemical detection of highly electronegative heavy metals such as manganese and zinc by anodic stripping voltammetry were investigated. Hydrolysis at the auxiliary electrode is a critical challenge in such electrochemical sensors as its onset severely limits the ability to detect electronegative metals. The described of sensors for the first time permit reliable and sensitive detection of the highly electronegative manganese. The favorable performance of the bismuth electrode coupled with its environmentally friendly nature make the described sensor attractive for different 2 applications. With further development and integrated sample preparation, the sensors may be converted into a point-of-care platform for monitoring heavy metals in blood (e.g. assessment of manganese exposure) (Preetha *et al,* 2011; Larisa *et al,* 2011).

Clay-modified platinum electrodes were prepared using naturally occurring Jordanian silicates, kaolinite and montmorillonite. Modified electrodes, which prepared using spin-coating procedures, were used for the selective and sensitive determination of Cu^{2+} and Hg^{2+} at ultra trace levels. Prior to clay deposition onto Pt

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surface, the extent of uptake of different organic and inorganic compounds were tested for kaolinite; the adsorption parameters for Cu^{2+} and Hg^{2+} were described using the popular Langmuir isotherm. Cyclic voltammetry and differential pulse voltammetry, combined with anodic stripping voltammetry, were employed for the qualitative and quantitative analysis of the tested cations. The modified electrodes showed a remarkable selectivity and sensitivity for Cu^{2+} and Hg^{2+} ions in natural water. Using montmorillonite-modified platinum electrodes, very low detection limits for cations were reached, 2.0×10-7 and 3.0×10-9 mol L-1 for Hg^{2+} and Cu^{2+}, respectively (Ayman *et al*, 2009).

In this work The interfering effect was studied of Mn(II) in different heavy metals such as Cu (II), Hg(II) and Cd(II) using different modified solid working electrodes as a good sensor electrode choosing in the study.

MATERIAL AND METHODS

Materials:

CNT (Fluka, 98%) and C_{60} (Fluka, 98%). Other chemicals and solvents were used of annular grade and as received from the manufacturer. Distilled water was used for the preparation of aqueous solutions. All solutions were deairated with oxygen free nitrogen gas for 15 minutes prior to making the measurement.

Instruments:

Electrochemical workstations of Bioanalytical System Inc. USA: Models BAS CV 50W with potetiostate driven by electroanalytical measuring software was connected to PC computer to perform cyclic voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire were used as a reference and counter electrode respectively (Instruction manual, 1996).

The working electrodes used in this study were GC electrode and modified GCE with CNT by mechanical attachment method (CNT/GCE) (Scholz and Lange 1992; Tan *et al,* 2000). Another modified electrode with C60 has evaporated on the GCE (C60/GCE) (Tan *et al,* 2003). C60/Li^+/GCE and CNT/Li^+/GCE were prepared by the doping of Li^+ ion on to C60/GCE and CNT/GCE via 10 potential cycling between +600 to -600mV in presence of 0.1M LiOH during cyclic voltammetry. A platinum wire (1mm diameter) counter electrode and an Ag/AgCl (3M NaCl) reference electrode were used in CV analysis.

Electrodes:

There are two methods for modification of working solid electrodes:

1. A Mechanical Attachment technique (MA): was used which involved the pressing of a clean GCE surface onto a few mg of CNT powder placed on a filter paper.
2. Solution evaporation technique: This method includes application of a 2 µL of saturated C_{60} in acetonitrile and subsequently dried by hot air blower before placing in voltammetric cell.

Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) the fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 kV. The scanning electron photographs were recorded at a magnification of 1000X to 6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 minutes before being coated with gold particle using SEM coating unit baltic SC030 sputter Coater. SEM was used to examine the morphology of CNT microcrystals by mechanical attached on a graphite electrode surface before and after electrolysis by cyclic voltammetry. Figure 1a and 2a are SEM of CNT/Li^+ and C_{60}/Li^+ respectively, attached and evaporated before electroanalysis with ions on to a 6 mm diameter basal plane graphite electrode which exhibits an array of microcrystals with 0.1-2 µm diameter. Figure 1b and 2b are SEM of CNT and C_{60} respectively, on a graphite electrode after electroanalysis with Mn(II).

RESULTS AND DISCUSSION

Effect of Different Modified Electrodes:

Figure 3 shows that the redox peaks of Mn^{2+} were considerably enhanced by 4-5 times, with almost a 200 mV peak shifting towards the origin, when the CNT/Li^+/GCE electrode was used in comparison with the C60/Li^+/GCE and GCE. The result confirms the electro-catalytic activity of CNT was also exerted on the redox of Mn (II) under the conditions of cyclic voltammetry. The degree of sensitivity/electro-catalytic response for the different electrodes increases in the order of:

CNT/Li^+/GCE > C_{60}/Li^+/GCE > GCE

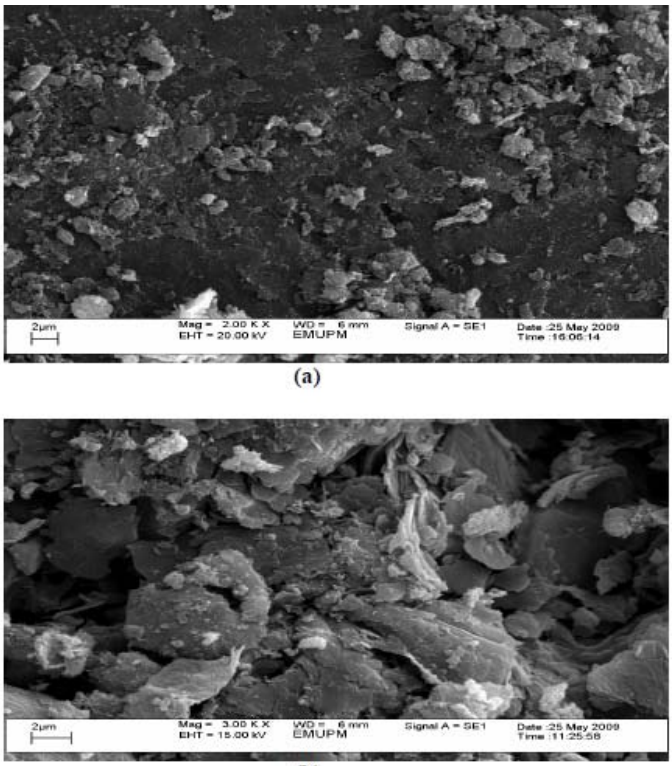


Fig. 1: Scanning electron micrographs of CNT/Li^+ microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis with Mn(II)

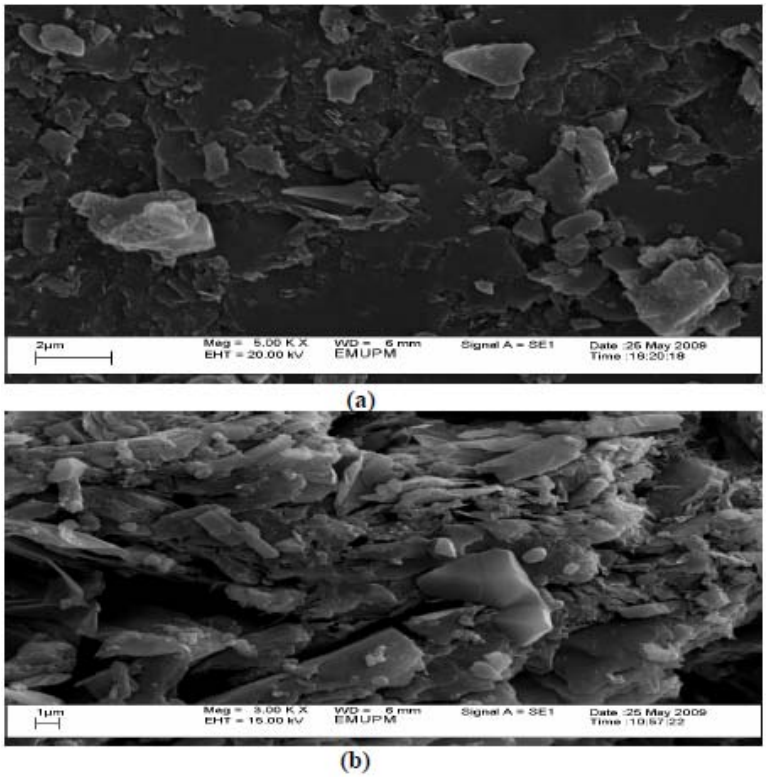


Fig. 2: Scanning electron micrographs of C_{60}/Li^+ microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis with Mn(II)

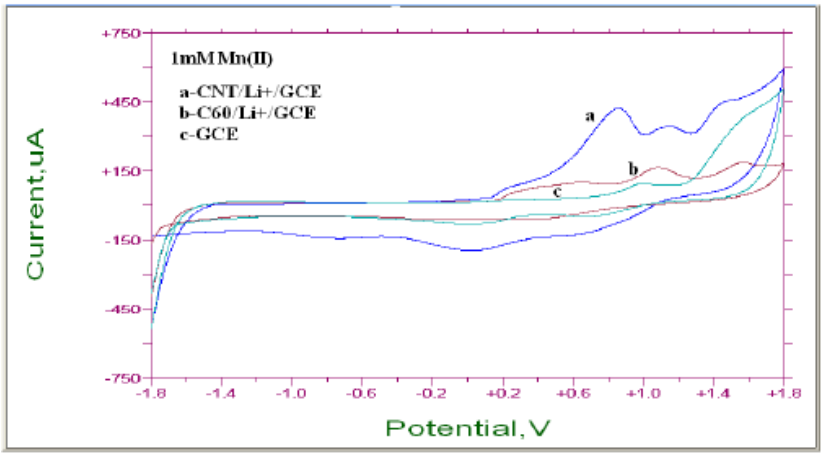


Fig. 3: Cyclic Voltammograms for the redox current at different modified GCE in 1mM Mn(II) with 0.1 M KCl as supporting electrolyte versus Ag/AgCl as reference electrode and scan rate 100mVsec^{-1}

Interference Of Heavy Metals Study:

Using modified C_{60}/Li^{+}/GCE:

Possible interference of some metals in the voltammetric determination of 2mM Mn^{2+} was studied by addition of the interfering ion to a solution containing 2mM of Hg^{2+}, Cd^{2+} and Cu^{2+} using the optimized conditions at pH2. The results in table 1 show positive interference of Hg^{2+}, Cd^{2+} and Cu^{2+} on the reduction peak of Mn^{2+} by different effect for reduction current and potential at C_{60}/Li^{+}/GCE.

Table:1 Effect of different heavy metals on reduction peaks of 2mM Mn^{2+} at pH 2 using C_{60}/Li^{+}/GCE versus Ag/AgCl.

Heavy Metals	Ipr(I)uA	Ipr(II)uA	Epr(I)mV	Epr(II)mV
Mn^{2+}, 2mM	-300	-150	+700	+200
Hg^{2+}, 2mM	-380	-320	+800	0
Cd^{2+}, 2mM	-60	-54	+650	0
Cu^{2+}, 2mM	-100	-788	+450	-1220

The interfering effect were investigated for metal ions in pH2 with Mn^{2+} using the modified electrode C_{60}/Li^{+}/GC, the two peaks of Mn^{2+} when added to 2mM Hg^{2+} causes to shift the first reduction peak from +700 to 800mV and second reduction peak from 200 to 0mV with increasing the current to two folds. In contrast, the interfering of Cd^{2+} on reduction peaks of Mn^{2+} decreased the current for both reduction peak and shifting the second peak to 0mV potential, also when used Cu^{2+} causes the same interferences to decrease the current for the first peak and shifted to lower potential, but the second reduction peak increased four folds and shifted to the lower negative potential. This means that the all metals used are a much high affinity for Mn^{2+} ion when used C_{60}/Li^{+}/GCE it appears that Hg^{2+} ion also take part as in the case of C_{60} used as an electro-catalysis for the reduction of Mn^{2+} to Mn^{0}.

The interference was carried out using 1:1 ratio of each metal ion (Hg^{2+}, Cd^{2+} and Cu^{2+}) possibly coexist with Mn (II). Insignificant interference was observed when Hg^{2+}, Cd^{2+} and Cu^{2+} coexist in the sample, indicating that these species did not really affect the determination of manganese. However significant interference was observed from Cd^{2+}, Cu^{2+}. Copper has the strongest effect on the determination of mercury by cyclic voltammetry in the potential range from +0.4 to +0.6 V, which makes the measurement of the CV current of mercury difficult. Copper was reported to have interference with electrochemical sensor based on conformational change mediated by Hg^{2+} coordination.

Hg^{2+} at C_{60}/Li^{+}/GCE:

As a result, mercury Hg^{2+} has been interference with reduction peaks of Mn^{2+}, which is shifted to +80 and 0mV when mixed in to ratio 1:1, and increased the current about four folds, also the influence of AA on the reduction peaks shifted to +75 and +5mV respectively, with increased current to nearly five folds.

It has been conjectured that the critical concentration of Mn^{2+} (0.7 – 0.8mM) when added to 2 mM Hg^{2+} causes decrease in the current of second peak of about two folds and shifted potential from +40 to +20mV.

The influence of oxidation peak of Hg^{2+} is increased in current of about four folds and shifted from +30 to +15mV at critical concentration (0.7- 0.8mM Mn^{2+}) as show in Figure 4.

However, the interference between Mn^{2+} and Hg^{2+} produced the complicated compound of Mn and Hg with structure form as in the following schema 1 (Cotton and Wilkinson 1998).

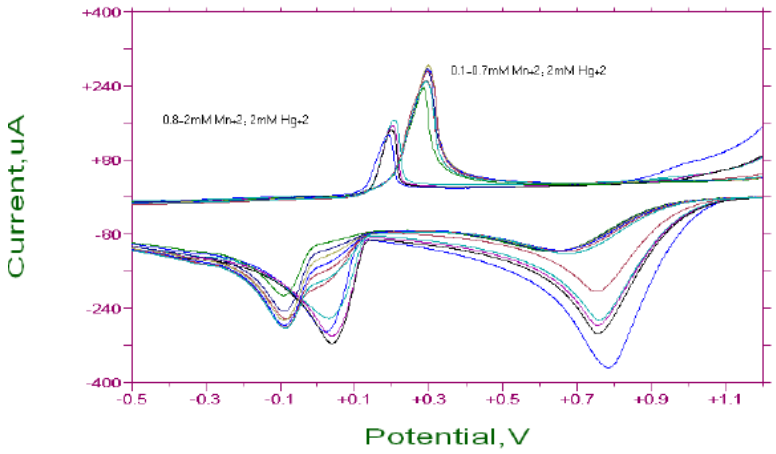
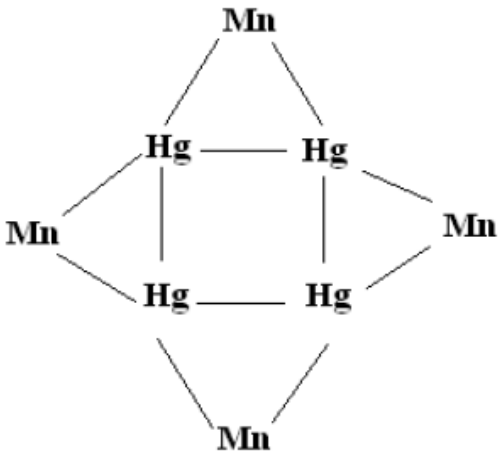


Fig. 4: Voltammogram for effected of high concentration Mn^{2+} on the Hg^{2+} peak and Mn^{2+} using C_{60}/ Li^{+} /GCE and 2mM Hg^{2+} : 2mM $Mn^{+2.}$



Scheme (1)

Cd^{2+} at C_{60}/Li^{+}/GCE:

There are two peaks for Cd^{2+} at-80 and -70mV for reduction and oxidation respectively, when C_{60}/Li^{+}/GCE is used. While the reduction of Cd^{2+} peaks disappeared. The oxidation peak of Cd^{2+} is shifted to -80mV and a new oxidation peak appears at +50mV with high current for Mn^{2+}. Thus, the oxidation reduction process of Mn^{2+} has effect of Cd^{2+} ions.

Cu^{2+} at C_{60}/Li^{+}/GCE:

The influence of Cu2+ ion on Mn2+ is not clear voltammetry except the effected on current against the concentration.

Using modified CNT/Li^{+}/GCE:

The interference at modified electrode CNT/Li^{+}/GCE of some metals in the voltammetric determination of 2mM Mn^{2+} was studied by addition of the interfering ion to a solution containing 2mM of Hg^{2+}, Cd^{2+} and Cu^{2+} using the optimized conditions at pH2.

Results in table 2 show positive interference of Hg^{2+}, Cd^{2+} and Cu^{2+} on the reduction peak of Mn^{2+} by increasing the reduction current with 3 folds and shifting to lower potential.

Table 2: Effect of different heavy metals on reduction peaks of 2mM Mn2+ at pH 2 using CNT/Li+/GCE.

Heavy Metals	Ipr(I), uA	Ipr(II), uA	Epr(I), mV	Epr(II), mV
Mn^{2+}, 2mM	-160	-110	+500	-140
Hg^{2+}, 2mM	-307.7	-238.5	0	-160
Cd^{2+}, 2mM	-215.4	-546.2	+400.5	-1373.9
Cu^{2+}, 2mM	-211.5	-769.2	+472.5	-1220.9

The two peaks of Mn^{2+} when added to 2mM Hg^{2+} causes to shift the first reduction peak from +500 to 0mV and second reduction peak from -140 to -160mV with increasing the current to three folds. While the interfering of Cd^{2+} on reduction peaks of Mn^{2+} increased the current of the second reduction peak and shifting to high lower potential, also when used Cu^{2+} causes the same interferences to increase the current of the second reduction peak to three folds. This means that Hg^{2+} is a much higher affinity for Mn^{2+} ion for other metal ions and it appears that Hg^{2+} ion also take part as in the case of CNT used as an electro-catalysis for the reduction of Mn^{2+} to Mn.

Hg^{2+} at CNT/Li^{+}/GCE:

The determination of Mn^{2+} was studied by addition of the interfering ion to a solution containing 2mM of Hg^{2+}, Cd^{2+} and Cu^{2+} using the optimized conditions. The interfering effect were investigated for metal ions in pH2 with Mn^{2+} using the modified electrode CNT/Li^{+}/GC, the two peaks of Mn^{2+} when added to 2mM Hg^{2+} causes to shift the first reduction peak from +50 to 0mV and second reduction peak from -140 to -160mV with increasing the current to three folds. While the interfering of Cd^{2+} on reduction peaks of Mn^{2+} just increase the current of the second reduction peak, also when used Cu^{2+} causes the same interferences to increase the current of the second reduction peak to three folds. This means that Hg^{2+} is a much higher affinity for Mn^{2+} ion for other metal ions and the interference of Hg^{2+} used as an electro-catalysis for the reduction of Mn^{2+} to Mn.

ACKNOWLEDGMENT

The authors wish to thank chemistry department, Faculty of science, at University Putra Malaysia for the provision of research facility.

Conclusion:

Interferences studies of Mn^{2+} with heavy metals indicated that the some metals effected on the conductivity of Mn^{2+} with this metals. The sensing characteristics of the different modified electrodes in this study for interference of Mn^{2+} in different heavy metals ion (Hg^{2+}, Cd^{2+} and Cu^{2+}), it founds that CNT/Li^{+}/GCE is more sensing than other electrodes at this study.

REFERENCES

Ayman, A.A., Y.S. Al-Degs and N.A.A. Al-Rabady, 2009. Selective Electrochemical Detection of Toxic Heavy Metals at Ultra Trace Levels using Natural Clay-Modified- Electrode, Eurasian J. Anal. Chem., 4(3): 245-256.

Cotton, F. and G. Wilkinson, 1988. Advanced Inorganic Chemistry, fifth edition, John Wiley and Sons, US.

Gazelle, L. and Turdean, 2011. design and development of biosensors for the detection of heavy metal toxicity. international journal of electrochemistry, 10(4061): 343125-40.

He, J.L., L. Qua, S. Hub, T. Zhana, C. Zhaoa and W. Suna, 2010. sensitive and simple electrochemical detection of lead(ii) with carbon ionic liquid electrode, Journal of the Chinese Chemical Society, 57: 1367-1373.

Instruction manual, CV 50W, version 2, Bioanalytical system Inc. USA (1996).

Larisa, L., R. Paolesse, C.D. Natale, A.D. Amico and B. Alberto, 2011, potentiometric polymeric film sensors based on 5,10,15-tris(4-aminophenyl) Porphyrinates of Co(II) and Cu(II) for Analysis of Biological Liquids, International Journal of Electrochemistry, 2011, 1-8.

Martínez-Huitle, C.A., N.S. Fernandes, M. Cerro-Lopez, M.A. Quiroz, 2010. determination of trace metals by differential pulse voltammetry at chitosan modified electrodes, Portugaliae Electrochimica Acta, 28(1): 39-49.

Preetha, J.R., A. Wilson, J.H. Erin, N.H. William, R.I. Papautsky, 2011. Lab-on-a-chip sensor for detection of highly electronegative heavy metals by anodic stripping voltammetry, Biomed Microdevices, 10(1007): 9539-9548.

Qiongyan, L., F. Wang, Y. Qiao, S. Zhang, Y. Baoxian, 2010. polyaniline langmuir–blodgett film modified glassy carbon electrode as a voltammetric sensor for determination of ag+ ions, electrochimica acta, 55(5): 1795-1800.

Scholz, F. and B. Lange, 1992. Abrasive stripping voltammetry - an electrochemical solid state spectroscopy of wide applicability, Trends in Analytical Chemistry, 11: 359-367.

Shenghui, Z. and W. Huang, 2001. simultaneous determination of Cd2+ and Pb2+ using a chemically modified electrodes, Journal of Analytical Sciences, 17: 983-985.

Stefanut, M.N., I. David, Z. Stanoiev, C. Macarie, 2007. The Monitoring of Heavy Metals in Fruits, Chem. Bull., 52(66): 1-2.

Tan, W.T., E. Lim and A. Bond, 2003. Voltammetric studies on microcrystalline C60 adhered to an electrode surface by solvent casting and mechanical transfer methods J. Solid State Electrochem., 7: 134-140.

Tan, W.T., G.K. Ng and A.M. Bond, 2000. Electrochemical of microcrystalline tetrathiafulvalene at an electrode solid aqueous K Brinterface, Malaysian J. Chem., 2: 34-42.

Xueji, Z., J. Huangxian and J. Wang, 2008. Electrochemical Sensors, Biosensors and Their Biomedical Applications, Academic Press is an imprint of Elsevier, USA, First edition.