© 2017 IJSRST | Volume 3 | Issue 6 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Scienceand Technology

Electrochemical Sensor for the Determination of Hydrazine Using MWCNT/Dopamine Dithiocarbamate Modified Electrode

J. Kavitha, M. Devendiran, K. Krishna Kumar, S. Sriman Narayanan*

Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai-600025, Tamil Nadu, India

ABSTRACT

An electrochemical sensor for the determination of hydrazine was developed using MWCNT/Dopamine dithiocarbamate (DDTC) modified electrode. DDTC was prepared using Dopamine and carbon disulphide in ammoniacal medium. The formation of DDTC was confirmed by FTIR spectroscopy. A modified electrode was prepared using the DDTC and was characterized by cyclic voltammetry. Hydrazine was found to undergo electrocatalytic oxidation with this modified electrode. Under optimal conditions, the modified electrode showed good performance for the electrocatalytic oxidation of hydrazine. The modified electrode exhibited a linear range from 1.9M to 740.7 M with a correlation coefficient of 0.9984 for the determination of hydrazine. Hydrodynamic and chronoamperometric experiments have revealed that the modified electrode can be used for the determination of Hydrazine in flow systems.

Keywords: Rapid Development, Effectiveness, Assessment, Monitoring, Management, Planning

I. INTRODUCTION

Hydrazine and its derivatives are widely used in chemical and pharmaceutical industries. They are mainly used as antioxidants, corrosion inhibitors, explosives, fuel cells, pesticides, herbicides, dyes, emulsifiers, catalysts, and oxygen scavenger [1–5]. They find widespread applications because of the strong reducing nature of the compound in addition to their alkalinity and hygroscopicity. However, hydrazine is harmful to the environment and human health. It was reported that hydrazine can damage even DNA in addition to liver and kidney [6]. Hydrazine is highly neurotoxic, carcinogenic and unstable. It causes high irritation, temporary blindness, dizziness, dermatitis, bronchiotitis and affects central nervous system [7,8]. The World Health Organization has identified hydrazine as a potent carcinogen with a threshold limit of 10 ppb [9]. Because of these considerable toxicological effects and industrial significance, there is a growing need to establish a reliable, sensitive and selective analytical method for the determination of trace levels of hydrazine. A number of analytical methods have been developed for the determination of hydrazine such as luminescence [10] spectrophotometry [11], High Performance Liquid Chromotography[12], capillary electrophoresis [13], flow Injection analysis [14], spectrofluorimetry[15], gas chromotography- mass spectrometry [16], ion chromatography [17] and electrochemical methods [8].

Majority of the above-mentioned techniques are time consuming whereas electrochemical techniques are fast, simple, real time detection, easy operation, high sensitivity and low detection capability. Chemically modified electrodes (CMEs) with suitable redox mediators have assumed greater significance due to their inherent advantages such as reduction in over potential and high sensitivity. Hence CMEs have been used for hydrazine determination.

Ceria nanoparticle in mesoporous carbon as a novel electrochemical sensor has been reported for the determination of hydrazine [18]. Simultaneous determination of hydrazine and hydroxylamine has been reported based on fullerene functionalized CNT/IL nanocomposite[19]. Hydrazine determination has also been reported using benzylamine functionalized graphene supported palladium modified electrode [20]. Recently a new in-situ synthesized ternary CuNPs-PANI-GO nanocomposite for selective detection of

IJSRST173666 | 02August 2017 | Accepted: 10August 2017 | July-August-2017 [(3)6 :227-232]

carcinogenic hydrazine has been reported [9]. From our laboratory also we have reported CMEs for the determination of Hydrazine. Nickel hexacynoferrate modified electrode was used for hydrazine determination [21]. Manganese hexacynoferrate modified graphite wax composite electrode has been used as an amperometric sensor for the determination of hydrazine [22]. A surface modified electrode has been used for the amperometric determination of hydrazine [23]In continuation of our work in the development of CMEs for the determination of hydrazine, we have used a new compound namely Dopamine dithiocarbamate as a redox mediator to develop a chemically modified electrode for the determination of hydrazine.

MWCNT has also been used along with the redox mediator as it provides larger surface area and also enhances the conductivity of the surface [24]. The electrochemical behavior of the MWCNT/DDTC modified electrode has been studied by Cyclic Voltammetry (CV) and the application of the modified electrode for the electrocatalytic oxidation of hydrazine by CV and chronoamperomerty has also been studied. The results have shown that the modified electrode has provided a better mediating platform for the electrocatalytic oxidation and determination of hydrazine.

II. EXPERIMENTAL

A. Chemicals and Reagents

Graphite rods (~3mm dia) and Dopamine hydrochloride were purchased from Aldrich, Germany. Hydrazine and Carbon disulphide were purchased from Merck. All other chemicals used were of Analytical grade and used without further purification. All solutions were prepared using double distilled water. Phosphate buffer solution of pH 6 was used as supporting electrolyte.

B. Instruments

All the electrochemical experiments were carried out using electrochemical work station (CHI 400A, USA) with a three electrode cell set-up. Standard Calomel electrode was used as the reference electrode the Pt wire as the counter electrode and the modified electrode as the working electrode. All experiments have been carried out at room temperature. FTIR spectra were obtained using JASCO (FT-IR 460 Plus, Japan) spectrometer.

C. Preparation of DDTC

Dopamine Dithiocarbamate was synthesized by following the reported method [25] with slight modification. In short, 0.5 mmol of Carbon disulphide and 0.5 mmol of NH_4OH were added to 10 ml of ethanol and to this mixture, 0.5 mmol of Dopamine was added. The mixture was stirred for 2 hours in ice bath and then for 3 hours at room temperature. The dopamine dithiocarbamate formed in the solution was obtained in solid form after evaporation of the solution.

D. Preparation of MWCNT/DDTC modified electrode

The preparation of MWCNT/DDTC modified electrode involves three steps as follows. In the first step PIGE was prepared using graphite rod following a reported procedure [26] and used for electrode modification. One end of the electrode was carefully polished with emery paper and then with 0.05µm alumina slurry, washed with distilled water and dried in air. Then, in the second step 10 µl dispersion of MWCNT (1 mg/ ml ethanol) was drop casted on the electrode surface and allowed to dry, then washed with doubly distilled water to remove unadsorbed MWCNT. Finally 10µl of dopamine dithiocarbamate in ethanol was drop casted on to the PIGE/MWCNT electrode and dried at room temperature. MWCNT electrode and DDTC electrode were also prepared by drop casing 10 µl of MWCNT and DDTC on the PIGE respectively for comparison.

III. RESULTS AND DISCUSSION

A. Characterization of Dopamine dithiocarbamate

The synthesized DDTC was characterized by FTIR spectroscopy and the FTIR spectrum of the compound is shown in Fig.1. The spectrum showed a peak at 936 cm^{-1} for the absorption of C-S group, a peak at 1080 cm^{-1} for C-H group, a peak at 2543 cm^{-1} for S-H group and a peak at 1498 cm^{-1} for C-N group. The presence of these peaks confirmed the formation of dopamine dithiocarbamate due to the reaction of the amine of dopamine and carbondisulphide.

The MWCNT/DDTC modified electrode was characterized by cyclic voltammetry. For comparison, the cyclic voltammograms of bare electrode, MWCNT electrode and DDTC modified electrode were recorded. The CVs obtained for these electrodes in PBS of pH 6 are shown in Fig.2. The bare electrode and the modified electrode did not exhibit any redox behavior in the potential studied (curve a & b respectively). The DDTC modified electrode without MWCNT has exhibited a redox behavior with a smaller current. The anodic peak was at 0.23 V and the cathodic peak was at 0.11 V with a ΔE_p of 0.12 V (curve c). On the other hand, the MWCNT/DDTC modified electrode has shown a well defined voltammogram with distinct peaks for oxidation and reduction. The oxidation peak was observed at 0.210V while the reduction peak was observed at 0.13 V with a $\Delta E_p$of 0.08 V. The presence of MWCNT on the electrode surface has reduced the ΔE_pvalue and has also enhanced the peak currents for the redox reaction of the dopamine dithiocarbamate. Thus the synergetic effect of MWCNT with the DDTC is seen in the voltammogram. Experiments have been carried out with various electrolytes such as KCl, KNO_3, LiCl, NaCl, NH_4Cl, $NaNO_3$, NH_4NO_3, $Ba(NO_3)_2$, acetate buffer solution and phosphate buffer solution. The results have shown that phosphate buffer solution is the most suitable background electrolyte for this modified electrode.

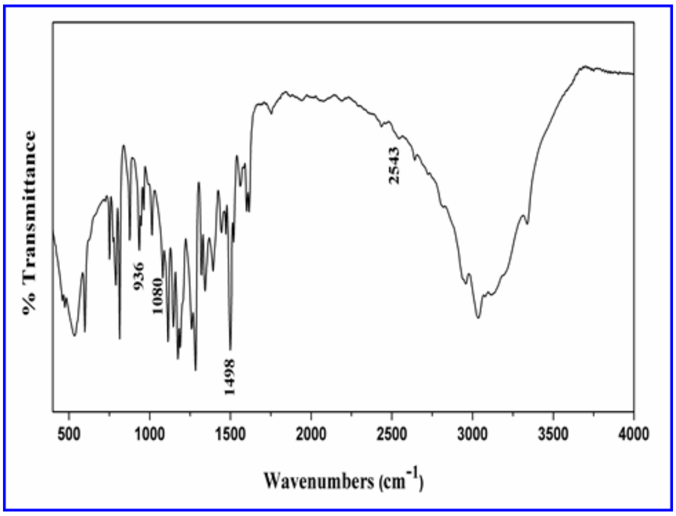

Figure 1. FTIR spectrum of dopamine dithiocarbamate

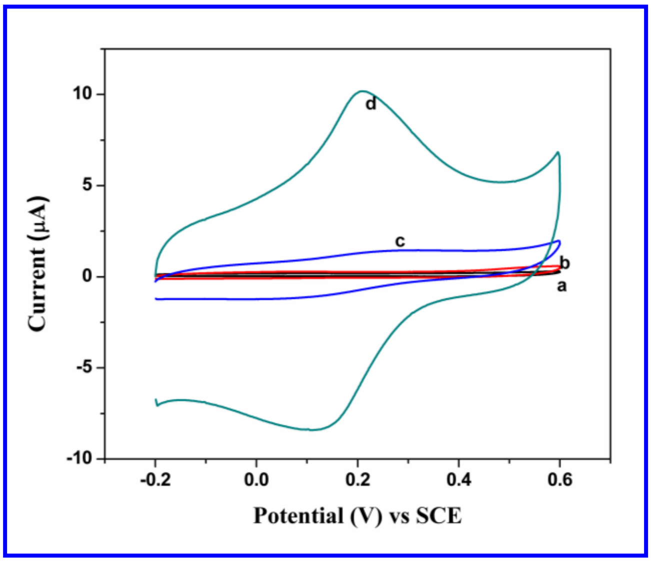

Figure 2. CVs of Bare (a), MWCNT (b), DDTC (c), MWCNT /DDTC (d) modified electrode 0.1M PBS (pH 6) at a scan rate of 50mV/s.

B. Electrocatalytic oxidation of Hydrazine at the MWCNT/DDTC Modified electrode

The electrocatalytic oxidation of hydrazine was studied using MWCNT/DDTC modified electrode by cyclic voltammetry in phosphate buffer (pH 6) as the background electrolyte. Figure 3 shows the results obtained for electrocatalytic oxidation of hydrazine with the MWCNT/DDTC modified electrode. Experiments have also been carried out with MWCNT modified electrode for comparison. Curve a and c show the CVs of MWCNT modified electrode and MWCNT/DDTC modified electrode respectively in the absence of hydrazine. The observation is similar to Figure 2 but in the presence of hydrazine, there is an increase in current for both the electrodes due to the oxidation of hydrazine. Curve (b) shows the oxidation current for hydrazine with the MWCNT electrode. It is seen that the oxidation took place around 0.5 V and the oxidation current was very less. On the other hand, with the MWCNT/DDTC modified electrode, the oxidation of hydrazine occurred around 0.25 V and a higher current was observed for the oxidation. Thus a reduction in the over potential of around 250 mV was achieved with the modified electrode and a higher current was also observed which could be attributed to the electrocatalytic oxidation of hydrazine. From this result, it can be inferred that the modified electrode can be used for the electrocatalytic oxidation and determination of hydrazine.

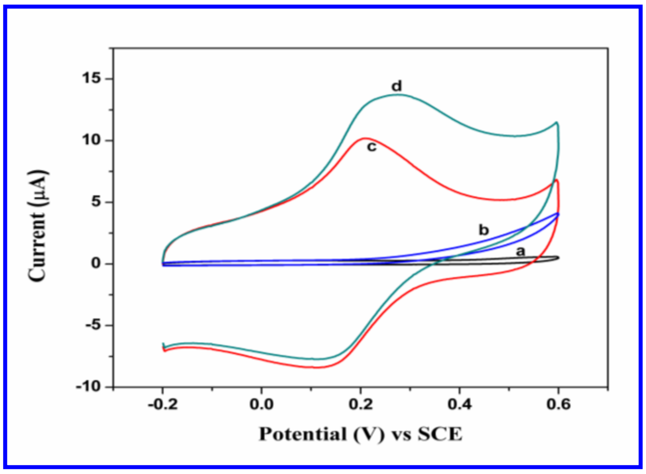

Figure 3. CVs of MWCNT (a), MWCNT /DDTC (c) modified electrode in absence and in presence (b & d) of 19.9 µM hydrazine in 0.1M PBS(pH 6) at a scan rate of 50mV/s.

C. Effect of pH

pH is one of the important parameter which affects the redox behavior of the electrocatalyst particularly if proton is involved in the electrocatalytic reactions. To study the effect of pH on the electrocatalytic oxidation of hydrazine by the modified electrode, experiments were carried out with phosphate buffer of different pHs ranging from 3-9. The results are shown in Fig.4. It is seen from the figure that as the solution pH increased from 3 to 6, a steady increase in the catalytic current was observed and beyond pH 6, a gradual decrease was observed.As higher peak current was observed at pH 6, the phosphate buffer of pH 6 was chosen as the background electrolyte for subsequent experiments.

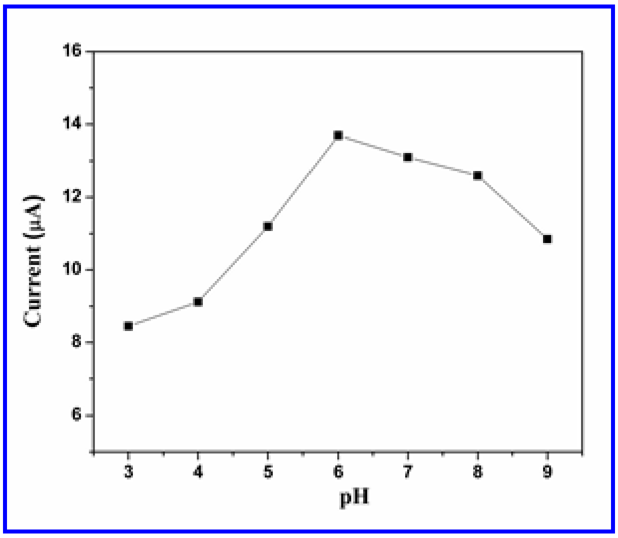

Figure4. Plot of pH versus Current response of MWCNT/DDTC modified electrode in presence of hydrazine (19.9 µM)

Cyclic Voltammograms have been recorded for various concentrations of hydrazine in phosphate buffer of pH 6. The current obtained were plotted against the concentration of hydrazine (Fig 5). It is seen from the figure that the catalytic current increased with increase in the concentration of hydrazine. A linear range for hydrazine from 1.9 µM to 740.7 µM was obtained with a correlation coefficient of 0.9984.

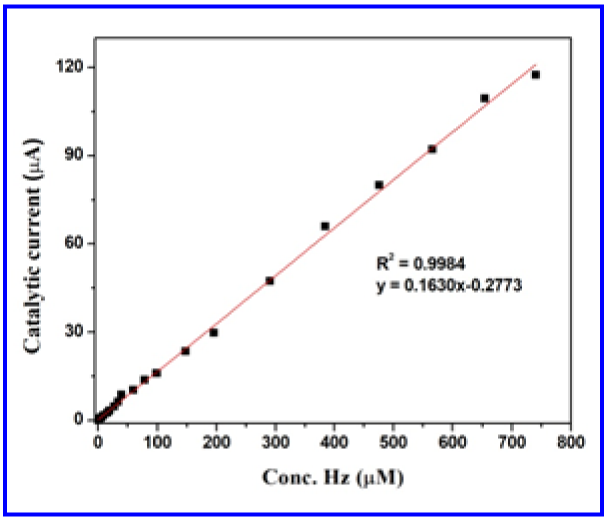

Figure5. Plot of catalytic current vs concentration of hydrazine from the range of 1.9 µM to 740.7 µM

D. Hydrodynamic voltammetry and Chronoamperometry

In order to evaluate the applicability of the modified electrode for the determination of hydrazine inflow systems, experiments were performed for the oxidation of hydrazine with the modified electrode in stirred solutions. The solution was stirred with a magnetic stirrer at a speed of 300 rpm. The catalytic current with the MWCNT/DDTC modified electrode was found to be maximum at 0.35 V. Hence a potential of 0.35 V was chosen as the optimum potential for carrying out chronoamperometric experiments for the catalytic oxidation of hydrazine.

Chronoamperometric experiment was carried out for electrocatalytic oxidation of hydrazine by fixing the potential of the electrode at 0.35 V and known amount of hydrazine was injected into the stirred solution at regular intervals of time. The results of chronoamperometric experiments are shown in Fig 6. The figure clearly shows that the MWCNT/DDTC modified electrode was responding well to the addition of hydrazine and reaches a steady state condition within a short period. The calibration graph for the chronoamperometric experiment is shown inFig 7. A linear range from 5.99 µM to 51.23 µM was observed with a correlation coefficient of 0.993. From the above studies, it is confirmed that this modified electrode can be used for the electrocatalytic oxidation of hydrazine in flow systems.

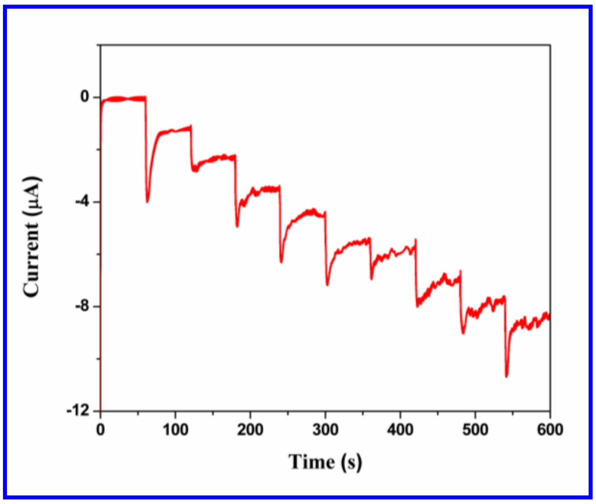

Figure 6. Amperometric response of MWCNT/DDTC modified electrode with increasing concentration of hydrazine at a fixed potential of 0.35V in 0.1 M PBS pH 6 under dynamic condition. (300µL of 0.001 M Hz at every 60 sec)

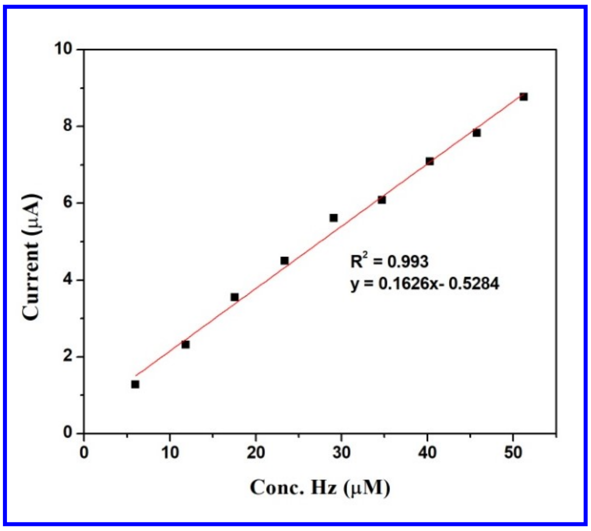

Figure7. Calibration plot for concentration of hydrazine

E. Stability of the MWCNT/DDT modified electrode

The long term stability of the modified electrode was checked for the oxidation of hydrazine for a period of two weeks by performing the oxidation of hydrazine everyday. A near constant current for the oxidation of hydrazine was obtained which indicated that the electrode is fairly stable. The electrode was kept in dark at 4° C when not in use.

IV. CONCLUSION

A MWCNT/DDTC modified electrode has been fabricated and characterized. The FT-IR studies have confirmed the formation of DDTC. The modified electrode was characterized by CV studies it has been used for the electrocatalytic oxidation of hydrazine. The electrode was also checked for its utility in flow systems and it was found that the electrode can be used for flow systems. The linear range of determination was found to be from 1.9 M to 740.7 □M with the correlation coefficient of 0.9984.

V. REFERENCES

[1]. A. Umar, S.K. Kansal, S.K. Mehta, Sensors and Actuators B : Chemical Highly-sensitive and selective detection of hydrazine at gold electrode modified with PEG-coated CdS nanoparticles, Sensors Actuators B. Chem. 188 (2013) 372-377. doi:10.1016/j.snb.2013.06.095.

[2]. S.K. Mehta, A. Umar, Talanta Highly sensitive hydrazine chemical sensor based on mono-dispersed rapidly synthesized PEG-coated ZnS nanoparticles, Talanta. 85 (2011) 2411-2416. doi:10.1016/j.talanta.2011.07.089.

[3]. M. Mazloum-ardakani, A. Khoshroo, Electrochimica Acta An electrochemical study of benzofuran derivative in modified electrode-based CNT / ionic liquids for determining nanomolar concentrations of hydrazine, Electrochim. Acta. 103 (2013) 77-84. doi:10.1016/j.electacta.2013.04.062.

[4]. A. Umar, M. Muzibur, S.H. Kim, J.F. Rusling, U.S. Schubert, A. Umar, et al., Zinc oxide nanonail based chemical sensor for hydrazine detection , 7345 (2008) 1-4. doi:10.1039/b711215g.

[5]. J. Liu, Y. Li, X. Huang, C @ ZnO nanorod array-based hydrazine electrochemical sensor with improved

sensitivity and stability, (2010) 8693-8697. doi:10.1039/c0dt00258e.

[6]. Y. Luo, X. Sun, Synthesis of Au nanoparticles decorated graphene oxide nanosheets : Noncovalent functionalization by TWEEN 20 in situ reduction of aqueous chloroaurate ions for hydrazine detection and catalytic reduction of, J. Hazard. Mater. 197 (2011) 320-326. doi:10.1016/j.jhazmat.2011.09.092.

[7]. M.U.A. Prathap, V. Anuraj, B. Satpati, R. Srivastava, Facile preparation of Ni (OH) 2 - MnO 2 hybrid material and its application in the electrocatalytic oxidation of hydrazine, J. Hazard. Mater. 262 (2013) 766-774. doi:10.1016/j.jhazmat.2013.09.050.

[8]. C.M.L. and Y.L. Yu Ding, Ying Wang, Lichun Zhang, Heng Zhang, Preparation of TiO 2 - Pt hybrid nanofibers and their application for sensitive hydrazine detection †, Nanoscale. 3 (2011) 1149-1157. doi:10.1039/c0nr00773k.

[9]. B. Vellaichamy, P. Periakaruppan, S.K. Ponnaiah, A new in-situ synthesized ternary CuNPs-PANI-GO nano composite for selective detection of carcinogenic hydrazine, Sensors Actuators BChem. 245 (2017) 156-165. doi:10.1016/j.snb.2017.01.117.

[10]. L. Cui, C. Ji, Z. Peng, L. Zhong, C. Zhou, L. Yan, et al., Unique Tri-Output Optical Probe for Speci fi c and Ultrasensitive Detection of Hydrazine, (2014).

[11]. V.A. Online, S. Subramanian, S. Narayanasastri, A. Reddy, K. Reddy, Doping-induced detection and determination of propellant grade hydrazines by a kinetic spectrophotometric method based on nano and conventional polyaniline using halide ion releasing additives †, RSC Adv. 4 (2014) 27404-27413. doi:10.1039/c4ra02296c.

[12]. J. Oh, H. Shin, Simple and sensitive determination of hydrazine in drinking water by ultra-high-performance liquid chromatography - tandem mass spectrometry after derivatization with naphthalene-2 , 3-dialdehyde, J. Chromatogr. A. 1395 (2015) 73-78. doi:10.1016/j.chroma.2015.03.051.

[13]. J. Liu, W. Zhou, T. You, F. Li, E. Wang, S. Dong, Detection of Hydrazine , Methylhydrazine , and Isoniazid by Capillary Electrophoresis with a Palladium-Modified Microdisk Array Electrode, Anal. Chem. 68 (1996) 3350-3353.

[14]. J. Zen, A.S. Kumar, H. Wang, A dual electrochemical sensor for nitrite and nitric oxide, (2000) 2-5. doi:10.1039/b008176k.

[15]. G.E. Collins, Sensitive , fluorescent detection of hydrazine via derivatization with 2 , 3-naphthalene dicarboxaldehyde, 284 (1993) 207-215.

[16]. J. Wang, M.P. Chatrathi, B. Tian, R. Polsky, Capillary Electrophoresis Chips with Thick-Film Amperometric Detectors : Separation and Detection of Hydrazine Compounds, Electroanalysis. 12 (2000) 691-694.

[17]. Chemical Studies on Tobacco Smoke Quantitative Analysis of Hydrazine in Tobacco and Cigarette Smoke, Anal. Chem. 46 (1974) 885-889.

[18]. Y. Liu, Y. Li, X. He, In situ synthesis of ceria nanoparticles in the ordered mesoporous carbon as a novel electrochemical sensor for the determination of hydrazine, Anal. Chim. Acta. 819 (2014) 26-33. doi:10.1016/j.aca.2014.02.025.

[19]. M. Mazloum-ardakani, A. Khoshroo, L. Hosseinzadeh, Simultaneous determination of hydrazine and hydroxylamine based on fullerene-functionalized carbon nanotubes / ionic liquid nanocomposite, Sensors Actuators B. Chem. 214 (2015) 132-137. doi:10.1016/j.snb.2015.03.010.

[20]. A. Ejaz, M.S. Ahmed, S. Jeon, Highly efficient benzylamine functionalized graphene supported palladium for electrocatalytic hydrazine determination, Sensors Actuators B. Chem. 221 (2015) 1256-1263. doi:10.1016/j.snb.2015.07.093.

[21]. D. Ravi Shankaran, S. Sriman Narayanan, Electrochemical determination of hydrazine based on chemically modified electrode, Res. J. Chem. Environ 5 (2001) 21.

[22]. D. Jayasri, S.S. Narayanan, Amperometric determination of hydrazine at manganese hexacyanoferrate modified graphite - wax composite electrode, J. Hazard. Mater. 144 (2007)348-354. doi:10.1016/j.jhazmat.2006.10.038.

[23]. A. Hajian, A. Abbas, A. Afraz, M. Naja, Electrosynthesis of high-density polythiophene nanotube arrays and their application for sensing of riboflavin, 199 (2014) 150-155.

[24]. M. Campus, Sensors and Actuators B : Chemical Hydrazine oxidation at gold nanoparticles and poly (bromocresol purple) carbon nanotube modified glassy carbon electrode, 196 (2014) 610-618. doi:10.1016/j.snb.2014.02.061.

[25]. K. Suresh-Kumar, W. Hui-Fen, One-pot synthesis of dopamine dithiocarbamate functionalized gold nanoparticles for quantitative analysis of small molecules and phosphopeptides in SALDI- and MALDI-MS, Analyst. 137 (2012) 1629-1638. doi:10.1039/c2an16008k.

[26]. F. Scholz, B. Lange, Abrasive stripping voltammetry - an electrochemical solid state spectroscopy of wide applicability *, Trends Anal. Chem. 11 (1992) 359-367. doi:10.1016/0165-9936(92)80025-2