

# Square Wave Anodic Stripping Voltammetric Determination of Zn (II) using Carbon Nanotubes / Novel Tetradentate Ligand Immobilized on PIGE Electrode

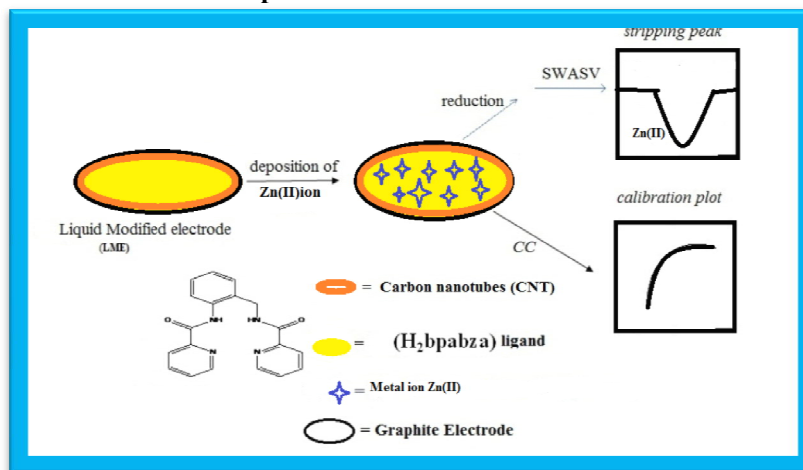
K.Sangeetha Selvan, S.Sriman Narayanan\*

Department of Analytical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai, Tamil Nadu, India

**ABSTRACT:** In this work, an anodic stripping voltammetric determination of Zn(II) with a Carbon nanotubes(CNTs) / novel tetradentate carboxamide ligand modified electrode is reported. The ligand was prepared by the condensation of 2-pyridinecarboxylic acid and 2-aminobenzylamine, with triphenyl phosphite as the activator and tetrabutylammonium bromide as the reaction medium. The ligand was characterized by Field emission scanning electron microscope method. The modified electrode was characterized by cyclic voltammetry, and electrochemical impedance spectroscopy. The modified electrode has provided an electrochemical sensing platform for determination of Zn(II) by anodic stripping voltammetry. The effects of experimental variables, such as deposition time, pH and supporting electrolytes on the determination of Zn(II) ion in 0.1 M sodium nitrate solution (pH 5) have been evaluated. Linear response from 2 to 210 nM for Zn(II) metal ion were achieved with the modified electrode. The LOD were 0.6nM for Zn(II) (S/N=3). The modified electrode was also successfully applied to the analysis of Zn(II) in real sample with good recovery, ranging from 100 - 102%.

**KEYWORDS:** Carboxamide ligand, Carbon Nanotubes (CNTs), chemically modified electrode, square wave anodic stripping voltammetry, Zn(II).

## Graphical Abstract



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## I. INTRODUCTION

Sensitive analytical techniques are required for the determination of trace metal ions present in the environment. Among the various toxic metal ions present in the environment, Zinc have tendency to accumulate in the body and may result in chronic damage Therefore, it is very important and highly valuable to develop a sensitive and simple analysis method for Zinc. Zinc is a chemically active metal and it readily forms alloys with other metals and these properties are utilised industrially in preparing a large number of zinc containing alloys and compounds. It is used in Chinese medicines drug called Milkvetch[1-4]. It is well known that zinc, as kind of nutritive elements, has an important role on mind, physical and immunologic function of mankind. Because of the widespread use of zinc, careful monitoring of zinc level in the environment is necessary to safeguard human life. Several methods have been used in trace metal analysis with varying degrees of success and convenience. At present several analytical methods have been proposed for the analysis of metal ions, such as potentiometry [5,6] atomic absorption spectrometry, UV-Vis spectrometry [8], surface enhanced raman spectrometry [9], inductively coupled plasma mass spectrometry [7-10] high performance liquid chromatography coupled with several detectors [11] and electrochemical techniques. Among these methods, attention is generally given to electrochemical techniques, for their advantages of portability, high-sensitivity and reproducibility. Especially, anodic stripping voltammetry using square wave is used frequently for anodic stripping analysis [12].

Carbon nanotubes (CNTs) have received increasing attention due to their high electrical conductivity, high surface area, significant mechanical strength and good chemical stability [13-16]. CNT modified electrode have been used as new material for detecting trace heavy metals by ASV[17]. In recent years, these has been a growing interest in the development of mercury free electrodes [18,19] for stripping analysis, as most of the reported stripping voltammetric methods are based on mercury electrodes like hanging mercury drop electrode (HMDE) or dropping mercury electrode (DME) or mercury film electrode (MFE) which have the ability to form amalgams with many metals.[20] Mercury based electrodes have been banned in several countries due to the strong toxicity, handling and disposal of mercury and its salts, and are unfriendly to the environment [21]. Hg has been replaced by less toxic or non-toxic electrode materials for the past few decades and a number of mercury-free electrodes have been reported [22-24]. A chemically modified electrode (CMEs) is most attractive alternatives to the mercury electrodes [25-27] for stripping analysis. The use of mercury electrodes for stripping analysis can be easily avoided by using chemically modified electrodes(CMEs). The important aspect in CMEs is the choice of modifier which confers special characteristics to the electrode surface [28]. Carboxamide ligand has been chosen as the modifier in this work as it readily complexes with transition metal ions like zinc, lead and cadmium.

Carboxamide ligands play key roles as chelating agents in main group and transition metal coordination chemistry, due to ease of synthesis, its role in biological systems and diverse therapeutic activities.[29-33] Numerous research groups have devoted their efforts to the synthesis and characterization of tetradentate unsymmetrical carboxamide ligands and their complexes with different metal ions like cobalt, lead, copper, etc.. Zhao et.al [34] have reported that square wave anodic stripping voltammetry (SWASV) promotes an improvement in low detection limit (LOD) resulting in high sensitivity and allowing the determination of trace metals at ppb level.

In this work, the carboxamide ligand has been synthesized as reported by Soraia Meghdadi, et.al., [35] by the reaction of 2-pyridinecarboxylic acid and 2-Aminobenzylamine, in tetrabutylammonium bromide medium with triphenyl phosphite as the activator. The CNT/ligand has been coated on the electrode by drop casting method to fabricate a mercury free electrode for the anodic stripping voltammetric determination of Zn(II). The ligand is used for the first time as sensing material on the surface of an electrode. This modified electrode was applied for the determination of Zn(II) in solution by SWASV. The modified electrode displayed higher peak current responses for zinc comparing the bare electrode. The modified platform exhibits good electrochemical stability and reusability. The applicability of this method was also evaluated by analyzing the recovery of the above ions in water and tablet sample.

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## II. EXPERIMENTAL RESULTS

### A. EXPERIMENTAL

#### 2.1. Chemicals and Reagents

Sodium nitrate solution 0.1 M (pH=5) solution was prepared using Double-distilled water (DDW) was used throughout the study. All reagents, 2-pyridinecarboxylic acid, 2-Aminobenzylamine, Tetrabutylammonium bromide (TBAB), and Triphenyl phosphite (TPP) were purchased from sigma Aldrich and used without further purification. The stock solutions of Zinc acetate (1 mM) were prepared by double-distilled water in standard flasks.

#### 2.2. Apparatus

All electrochemical measurements were performed using a CHI 660B potentiostat, (CH Instruments, USA). A conventional three-electrode system was used that consists of the carboxamide ligand/CNT modified electrode as the working electrode (3 mm dia), a platinum electrode was used as auxiliary electrode and (Ag/AgCl) saturated KCl electrode was an reference electrode. Solutions were stirred during the purging with high-purity nitrogen and preconcentration with a rotating PTFE pellet.

The morphology of carboxamide ligand/CNT on the electrode surface was investigated by Field emission scanning electron microscopy (FESEM) using a Hitachi SU-6600 microscope (Japan) with an accelerating voltage of 15kV without sputter coating. EDS analysis was done using Horiba E max X-ray analysis spectrometer. pH adjustments were carried out using a Digisun electronics system model pH -Meter. UV-Visible analysis was done using Cary 8453UV-Vis diode array spectrophotometer. FTIR was recorded using Cary 630 FTIR instrument.

#### 2.3. Synthesis of carboxamide ligand

The preparation of carboxamide ligand was carried out as previously reported [36] with slight modification. In brief, (10mmol) 3.1g triphenyl phosphite (TPP), (5mmol) 1.61g tetrabutylammonium bromide (TBAB), (10mmol) 1.231g 2-Pyridinecarboxylic acid and (5mmol) 0.611g 2-aminobenzylamine were placed in 25ml RB flask and heated in an oil bath. The reaction mixture was stirred vigorously for 20min at 120°C and heated until a viscous and homogeneous solution was formed. The resulting viscous solution was cooled to room temperature and then 10ml of methanol was added to get a clear solution by stirring, kept for drying under vacuum for 24h to get white crystal of the ligand.

#### 2.4. Fabrication of carboxamide ligand/CNT modified electrode

Paraffin impregnated graphite electrodes (PIGEs) of 4 cm length with a diameter of 3 mm were used for modification. The PIGEs were prepared as reported [36] by immersing the graphite rods into molten wax under vacuum until air bubble cease to evolve from the rods. After re-establishing atmospheric pressure, the graphite rods were removed before the solidification of paraffin. The PIGEs were then polished to a mirror like finish by rubbing over a finest quality of emery paper. The polished surface was then washed thoroughly with double distilled water. The 0.1mg of CNTs which are dispersion in 1ml of ethanol and 5 $\mu$ L of CNT was coated on the polished PIGE surface and allowed to dry, then carboxamide ligand which was dissolved in acetonitrile and 5 $\mu$ L of 0.001mm of carboxamide ligand was dropcasted on the CNT electrode surface and allowed to dry and washed with distilled water .

#### 2.5. Stripping voltammetry with carboxamide/CNT modified electrode for Zn(II) determination

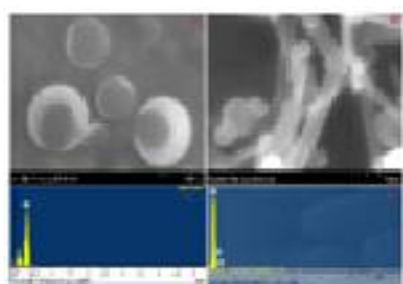
The anodic stripping voltammetric determination of Zn(II) was carried out in the following manner. A known amount of solution containing both Zn(II) was pipetted out into the electrochemical cell which was having 60mL of 0.1M NaNO<sub>3</sub> solution of pH 5. The ligand modified electrode was put on the sample solution and stirred for 240s for preconcentration of the metal ion on the electrode surface. Then the modified electrode was taken out washed and kept in fresh background electrolyte of NaNO<sub>3</sub> solution and reduced at a potential of -1.5V. A SWASV was recorded for the electrode with the frequency of 25Hz by scanning the potential from -1.5V to -1.0V. The amplitude and the potential steps were 25mV and 4mV respectively.

Although a number of reports on the determination of Zn(II) by anodic stripping voltammetry at different mercury based electrodes can be found in the literature, the toxicity and associated health hazards surrounding mercury could be avoided in the development of mercury free electrodes for anodic stripping analysis. Preliminary investigation with the carboxamide ligand/CNT modified electrode showed that the carboxamide ligand is a potential complexing agent and can be used for the preconcentration of Zn(II). Hence various parameters that can influence the anodic stripping voltammetric determination of Zn(II) such as medium for complexation, pH, preconcentration time, and reduction potential have been optimized. In addition, the UV-Visible, FTIR, NMR and Raman spectroscopy characterization of the ligand have also been carried out. The surface morphology of the modified electrode with the ligand and the EIS for the modified electrode have also been carried out and the details are given below.

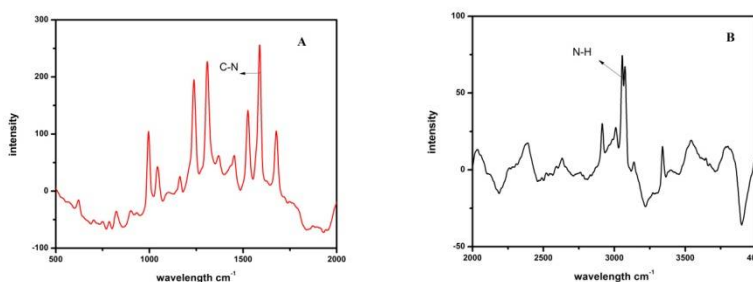
#### A. SPECTROSCOPY CHARACTERIZATION

The surface morphology of the bare/CNT and CNT/ligand modified electrode was recorded using FESEM. The SEM pictures of Carboxamide ligand/CNT modified electrode and bare/CNT electrode are shown in **Fig.1.A and B**. For bare electrode particles were homogeneously distributed throughout the electrode surface while carboxamide ligand modified electrode revealed rod shape structure on the electrode surface. The energy dispersive X-ray spectroscopy (EDS) analysis of modified electrode and bare electrode is shown in **Fig.1.C and D**. The C and N peaks were found on the carboxamide ligand/CNT modified electrode whereas, only C peak was found in bare/CNT electrode.

The Raman spectra of carboxamide ligand is shown in **Fig. 2. A and B**. The Raman spectrum of carboxamide ligand shows an absorption corresponding to the presence of free C-N group at  $1587\text{cm}^{-1}$ , and the presence of N-H group at  $3056\text{cm}^{-1}$  confirming the formation of carboxamide ligand.



**Figure.1.** FESEM images of (A) Bare/CNT electrode with 30.0kx magnification and (B) Carboxamide ligand/CNT modified electrode with 45.0kx magnification, (C) EDS spectrum of the CNT and (D) carboxamide/CNT modified electrode



**Figure.2.** (A) and (B) Raman spectra of carboxamide modified electrode.

#### B. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) STUDY OF MODIFIED GRAPHITE ELECTRODE

Electrochemical impedance spectroscopy (EIS) is an effective electrochemical method, which is used to study the interface properties of surface modified electrodes [37]. In EIS study, the surface changes on the electrode causes changes in AC impedance. This changes can be modulated according to Randle's equivalent circuit [38]. Randle's model  $R_s(CPE|R_{ct}Z_w)$ , where  $R_s$  is solution resistance,  $R_{ct}$  is the charge-transfer resistance and  $Z_w$  is Warburg impedance was sufficient to explain EIS data obtained. **Fig.3** shows Nyquist diagrams for bare and carboxamide/CNT modified electrode in 0.1 M acetate buffer solution containing  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution at a scanning rate of  $50\text{mVs}^{-1}$ . Equivalent circuit was fitted, and the ( $R_{ct}$ ) electron (or) charge transfer resistance was calculated. From Nyquist plot the  $R_{ct}$  values for the bare electrode and carboxamide/CNT modified electrode were estimated as  $9.77 \times 10^{-4}\text{K}\Omega\text{cm}^{-2}$ , and  $5.916 \times 10^{-4}\text{K}\Omega\text{cm}^{-2}$  respectively.

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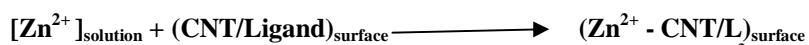
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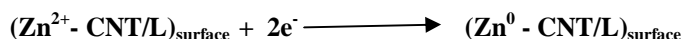
## C. STANDARD PROCEDURE OF MEASUREMENT

The determination of Zn(II) was performed as per the following procedure (**Scheme-1**)

**step:1** Zinc ion was first preconcentrated by immersing the modified electrode into 0.1M NaNO<sub>3</sub> Solution (pH-5) containing 50 nM of Zn(II) under open circuit condition (OCC) for 3mins to form complexes with carboxamide ligand (L).



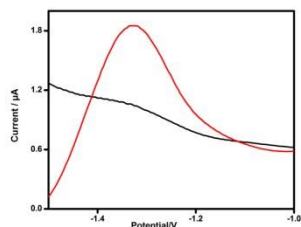
**step:2** A potential of -1.5V in 0.1M NaNO<sub>3</sub> solution was applied for the reduction of (Zn<sup>2+</sup> to Zn<sup>0</sup>)



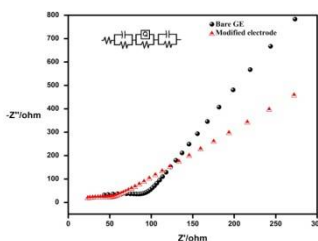
**step:3** The metal present on the electrode surface was anodically stripped by scanning the potential from -1.5V to -1.0V using square wave anodic stripping with optimized parameters (frequency 25Hz; amplitude 25mV; increment potential 4mV).



The metal ion on the electrode surface was removed by dipping in 0.1M EDTA solution for 60 sec with stirred condition. The metal ion from the electrode surface comes into the solution via EDTA forms complex with EDTA-Zn<sup>2+</sup> in pH 4.5 [43] the carboxamide ligand modified electrode was completely washed with distilled water. so that the electrode can be regenerated each time for further experiments. The result obtained is shown in **fig.4**. The above procedure was applied for both bare and modified electrodes.



**Figure.3.** Nyquist plot of electrochemical impedance spectra for bare and modified electrode in 0.1M ABS containing Fe(CN)<sub>6</sub><sup>3-/4-</sup>.



**Figure.4.** SWASV for 30 nM of Zn(II) on the bare /CNT and carboxamide/CNT modified electrode in 0.1M Sodium nitrate solution pH-5. Scan rate: 50mV/s.

## D. STUDIES ON EXPERIMENTAL VARIABLES ON THE ANODIC STRIPPING VOLTAMMETRY OF ZN(II)

In order to obtain a better sensitivity for the determination of Zinc(II) with carboxamide/CNT modified electrode, the different experimental conditions of SWASV were optimized such as supporting electrolyte, pH and preconcentration time.

### 3.4.1 Medium for preconcentration

Experiments have been carried out with different electrolytes of 0.1M solution of ABS buffer, KNO<sub>3</sub>, NH<sub>4</sub>Ac, NaNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> for the determination of Zn(II) 50 nM by SWASV. The pH was adjusted to 5 for complexation. A maximum stripping peak current was observed when 0.1M NaNO<sub>3</sub> solution was used as the medium for preconcentration.(**Fig.5.A**) Thus, to have a higher sensitivity with modified electrode towards Zn(II) determination NaNO<sub>3</sub> solution medium was chosen for preconcentration.

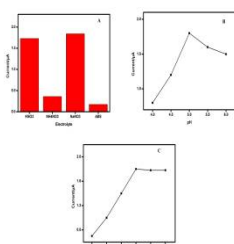
### 3.4.2 Effect of pH

The effect of pH on the stripping analysis of the modified electrode towards the determination of Zn(II) was also investigated by SWASV in 0.1 M NaNO<sub>3</sub> solution containing 50 nM of Zn(II) under open-circuit condition. The sensitivity of the anodic stripping voltammetric (ASV) analysis of metal ion through complexation with the chelating

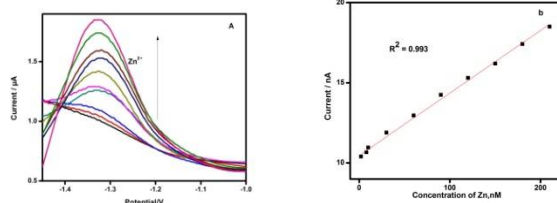
ligand is strongly dependent upon the pH and nature of the medium. The electrochemical response of the modified electrode towards the detection of the Zn(II) were initially studied by SWASV at different pHs using NaNO<sub>3</sub> solution. The variation of anodic stripping current response of Zn(II) with respect to pH of solutions are shown in **fig.5.B**. It can be seen that the stripping peak current increases with increasing the pH of the medium from 4 to 5, and then decreases with further increasing of the pH. Therefore, pH 5 was chosen as the optimum pH for the preconcentration of metal ion on the carboxamide/CNT modified electrode.

### 3.4.3 Effect of preconcentration time

The effect of preconcentration time on the stripping analysis towards the determination of Zn(II) with the modified electrode was also investigated by SWASV in 0.1 M NaNO<sub>3</sub> solution of pH 5 containing 50 nM of Zn(II) under open-circuit condition. The variations of anodic stripping peak current of Zn(II) with respect to the change in the preconcentration time in the range from 1 to 6 mins are shown in **Fig.5.C**. It is seen that the stripping peak current increases sharply within the first 5 min, and then shows a constant current, suggesting that the preconcentration of Zn(II) at the carboxamide/CNT modified electrode reaches saturation after 4 minutes. Taking sensitivity and the efficiency into account, a preconcentration period of 5 min was chosen for the other experiment.



**Figure.5.**Optimum experimental conditions Influence of (A) supporting electrolytes; (B) pH (C) deposition time on the Voltammetric response of the carboxamide/CNT modified electrode for 50 nM of Zn(II) ,deposition potential:-1.2V,frequency 25Hz;



**Figure.6.** SWASV responses (A) and the corresponding calibration plot (B) of the carboxamide/CNT modified electrode towards Zn(II) over a concentration range of (2 to 210) nM for Zinc by depositing for 240s in 0.1M sodium nitrate (pH -5) deposition potential:-1.2V,frequency 25Hz; amplitude,25mV; increment potential 4mV.

### 3.5. Calibration data

Under optimal conditions, the carboxamide modified electrode was applied for the determination of Zn(II) in 0.1M NaNO<sub>3</sub> solution. SWASV response towards Zn(II) at different concentrations was measured by preconcentrating the metal ion for 4mins on the electrode surface from 0.1M NaNO<sub>3</sub> solution of pH 5. The electrode was then removed from the metal ion solution, washed and kept in fresh background electrolyte of NaNO<sub>3</sub> solution and was reduced at -1.5V and then SWASV was recorded. **Fig.6.A**. shows the SWASV response of Zn(II) at different concentration ranging from 2 to 210 nM. The stripping peak current were linear with increasing concentration of the metal ion. The correlation equations were defined as  $Y=0.02x+0.9nM$ ,  $R^2= 0.993$  for Zn(II) respectively (Y: current/ $\mu A$ , x:concentration/ $\mu gL^{-1}$ ) the calibration curves are shown in **fig.6.B**. The limit of detection (LOD) was found to be 0.6 nM of Zn(II). Moreover, the detection limit obtained with the carboxamide/CNT modified electrode compares favorably with previously reported modified electrodes (**Table 1**). The results indicate that the proposed method shows high sensitivity for the detection of heavy metal.

**Table 1:** Limits of detection of Zn<sup>2+</sup> by anodic stripping voltammetry at CNT with ligand modified electrodes.

Modified	Linear range(nM)	LOD	Deposition time	Reference
Micro fab Bi-electrode	500-5000	166	600s	39
Bi-CNT electrode	2-100	12	240s	40
MWCNTs-NaDBS	5-100	0.9	240s	41
Bi-film electrode	10-100	0.7	180s	42
CNT/(Carboxamide)	2-210	0.6	240s	This work

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### 3.6. Repeatability, stability and interference studies

The modified electrode showed a long-term stability with no systematic differences in performance between the freshly prepared electrodes and electrodes stored for 3 weeks after preparation, in SWASV experiments with 40 nM for Zn(II) as no significant change in the current response was observed. The repeatability of the prepared electrode was investigated by successive addition (N=5) of 40nM of Zn(II) ion. A satisfied repeatability was received with RSD of 3.1% for Zn(II) ion.

Under optimized conditions, the electrochemical response for Zn(II) ion was detected in presence of 10-fold concentrations ratio of Ni(II), Cu(II), Fe(II), Hg(II), Pb(II) and Co(II) ions. The result indicates that these metal ions almost had no interference for the detection of Zn(II) ion because the peak current decreases less than 5% deviation [44]. Therefore the prepared electrode has a excellent interference studies, stability and repeatability for the determination of Zn(II) .

### 3.7. Analysis of real sample

The carboxamide/CNT modified electrode was employed to the determination of Zn(II) in mineral water and tablet (Faa 20) samples using the method of standard addition. A known amount of Zn(II) was added to the mineral water and tablet , the samples were analyzed two times and the anodic stripping currents were measured. The mean recovery (%  $\pm$ SD) of the metal ions was calculated, and the values are summarized in **Table.2**. The results obtained for the proposed method is very satisfactory with an average recovery of 100% - 102% for Zn(II). This indicates that the proposed carboxamide modified electrode is suitable for the determination of trace metal in mineral water and tablet samples.

**Table:2** Recoveries of metal ions in tablet and water sample

Sample	Metal	Added(nM)	Found(nM)	Recovery(%)
Tablet (Faa 20)	Zn (II)	30	30.5 $\pm$ 0.01	101
		50	50.7 $\pm$ 0.02	102
Mineral water	Zn(II)	70	70.4 $\pm$ 0.01	101
		90	90.3 $\pm$ 0.02	100

## IV. CONCLUSION

In this work, a simple, reproducible and sensitive procedure has been developed for the simultaneous determination of Zn(II) ion using a carboxamide/CNT modified electrode. The results suggest that carboxamide ligand is a promising material which posses the advantages for stripping analysis in comparison with other suggested electrodes in detecting Zn(II) ion with detection limits in the range of nM, with high sensitivity and long term usage. It is found that the operational parameters such as pH, deposition time, supporting electrolyte, etc., systematically affected the stripping current. The carboxamide/CNT modified electrode showed a good selectivity and satisfying reproducibility with the RSD of the stripping signal less than 3% for Zn(II) in mineral water and tablet confirming that carboxamide/CNT modified electrode can be applied towards the metal detection in real sample.

## REFERENCES

- [1] Marcelo Firmino de Oliveira Adelir Aparecida Saczk, Leonardo Luiz Okumura Æ Andre'a Pires Fernandes, Mercedes de Moraes Æ Nelson Ramos Stradiotto, Anal Bioanal Chem 380 (2004) 135–140.
- [2] Cecil K., Drinker M.D. 1937. J Am Med Assoc.; 108(26): 2241-2242.
- [3] Gupta S.K. 2002. Emergency Toxicology, Management of common poison, Narosha Publishing. House New Delhi. 72-73.
- [4] Onar A.N., Temizer A. Analyst 112 (1987)227-229
- [5] A.A. Ensafi, S. Meghdadi, A.A. Allafchian, J. Korean Chem. Soc. 51 (2007)324–330.
- [6] A.A. Ensafi, S. Meghdadi, A.A. Allafchian, IEEE Sens. J. 8 (2008) 248–254.

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(An ISO 3297: 2007 Certified Organization)

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- [7] D. Manivannan, V.M. Biju, Water Sci. Technol. 64 (2011) 803–808.  
[8] J.P. Cornard, A. Caudron, J.C. Merlin, Polyhedron 25 (2006) 2215.  
[9] Y. Ma, H. Liu, K. Qian, L. Yang, J. Liu, J. Colloid Inter. Sci. 386 (2012) 451.  
[10] S. Arpadjan, G. Celix, S. Taskesen, S. Gucer, Food Chem. Toxicol. 46 (2008) 2871.  
[11] M. Chen, L. Ma, X. Chen, Talanta 125 (2014) 78–86.  
[12] Xiulan Sun, Cai Li, Zaijun Yan, Zhilei Wei, Yinjun Fang, Guoxiao Ren, Yaru Huang, Electrochim. Acta 56 (2011) 1117–1122.  
[13] L.Fotouhi, S.Arabiyani, O.Moradlou, Anal.Bioanal.Electrochem 5(2013)283-290.  
[14] A. Peigney, Ch.Laurent, E.Flahaut, R.R.Bacsa, A.Rousset, Carbon 39 (2001) 507.  
[15] M.M.J.Treacy, T.W.Ebbesen, J.M.Gibson, Nature 381 (1996) 678.  
[16] P.M.Ajayan, T.W.Ebbesen, T.Ichihashi, S.Iijima, K.Tanigaki, H.Hiura, Nature 362 (1993) 522.  
[17] K.B.Wu, S.S.Hu, J.J.Fei, W.Bai, Anal. Chem. Acta 489 (2003) 215.  
[18] V.Izadkhah, A.Farmany, S.S.Mortazavi, J. Ind. Eng. Chem. 21 (2015) 994–996.  
[19] S.Chaiyo, O. Chailapakul, T.Sakai, N.Teshima, W.Siangproh, Talanta 108 (2013) 1–6.  
[20] H.Rashidi Nassab, M.Bakhshi, M.K.Amini, Electroanalysis 26 (2014) 1598-1605.  
[21] E. Gustafsson, Water Air Soil Pollut. 80 (1995) 99.  
[22] N. Lezi, C. Kokkinos, A. Economou, M.I. Prodromidis, Sens. Actuators B 182 (2013) 718–724.  
[23] Q.T. Cai, S.B. Khoo, Analyst 120 (1995) 1047–1053.  
[24] N. Spano, A. Panzaneli, P.C. Piu, M.I. Pilo, G. Sanna, R. Seeber, A. Tapparo, Anal. Chim. Acta 553 (2005) 201–207.  
[25] L. Chen, Z.H. Su, X. He, Y. Liu, C. Qin, Y.P. Zhou, Z. Li, L.H. Wang, Q.J. Xie, S.Z. Yao, Electrochem. Commun. 15 (2012) 34.  
[26] L.C.S. Figueiredo-Filho, B.C. Janegitz, O. Fatibeli-Filho, L.H. Marcolino-Junior, C.E. Banks, Anal. Methods 5 (2013) 202.  
[27] C.Kokkinos, A. Economou, Talanta 84 (2011) 696.  
[28] Daniele Merli, Stefano Protti, Matteo Labò, Maria Pesavento, Antonella, Talanta 151 (2016) 119-125.  
[29] F. Lebon, N. Boggetto, M. Ledecq, F. Durant, Z. Benatallah, S. Sicsic, R. Lapouyade, O. Kahn, A. Mouithys-Mickalad, G. Deby-Dupont, M. Reboud-Ravaux, Biochem. Pharmacol. 63 (2002) 1863.  
[30] N.A. Pulina, P.A. Mokin, V.V. Yushkov, V.V. Zalesov, T.F. Odegova, M.A. Tomilov, K.V. Yatsenko, Pharm. Chem. J. 42 (2008) 389.  
[31] D.K. Sau, R.J. Butcher, S. Chaudhuri, N. Saha, Mol. Cell. Biochem. 253 (2003) 21.  
[32] A.K. Patra, M.J. Rose, K.A. Murphy, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 43 (2004) 4487.  
[33] Q. Zhu, X. Wang, Z. Chu, G. He, G. Dong, Y. Xu, Bioorg. Med. Chem. Lett. 23 (2013) 1993.  
[34] Z.Q.Zhao, X.Chen, Q.Yang, J.H.Liu, X.J.Huang, Electrochem.Comm.23(2012)21-24.  
[35] Soraia Meghdadi, et.al., polyhedron 85 519-524 (2015).  
[36] F. Scholz, B. Meyer, Chem. Soc. Rev. 23 (1994) 341.  
[37] L. Zou, Y.F. Zhang, H. Qin, B. Yea, Electroanalysis 21 (2009) 2563–2568.  
[38] J.R. Macdonald, Impedance Spectroscopy, John Wiley & Sons, New York, 1987.  
[39] Preetha Jothimuthu, a Robert A. Wilson, b Josi Herren, a Xing Pei, a Wenjing Kang, a Rodney Daniels, c Hector Wong, c Fred Beyette, a William R. Heineman, b and Ian Papautsky, Electroanalysis. 2013 Feb; 25(2):  
[40] Gil Ho Hwang, Won kyu Han, Joon shik park, sung goon kang ,talanta 76 (2008) 301-308.  
[41] Yun Qing Tian, Nian Bing Li, Hong Qun Luo, Electroanalysis 2009, 21, No. 23, 2584 – 2589.  
[42] G Kefala, A Economou, Talanta, 61, 5, (2003), 603–610.  
[43] T.H.Degefa, B.Singh Chandravanshi, H.Alemu, Electroanalysis 11 (1999) 1305.  
[44] Jiali Wei, Duanguang Yang, Hongbiao Chen, Yong Gao, Huaming Li, Sens. Actuators B 190 (2014) 968–974.