Extractive differential pulse polarographic determination of copper and nickel
IV A Copper

Introduction

Copper is a reddish-colored metal with a high electrical and thermal conductivity. Copper is one of several metal ions that play an important role in the biological system. It plays a key role during cell respiration, in the blood of invertebrate animals and in the formation of haemocyanin. It is an important respiratory protein, found in the lymph of most animals belonging to phyla mollusca and arthropod. From the point of human health, it plays vital role in three physiological functions of prime importance. Copper is involved in the haemopoiesis, maintenance of vascular and skeletal integrity besides the structure and function of the central nervous system.

Copper occurs naturally in most vegetables, meat and grains. The study of copper in food items is having great concern, since it plays a detrimental role in the intrinsic mechanisms i.e., regulating vital biological processes. Over exposure to copper causes metallic taste, ptyalism, nausea, vomiting, epigastric burning and diarrhea. Heavy doses of copper cause a series of systematic toxic effects such as hemolytic, hepatic neurosis, gastro-intestinal bleeding, oliguria azoemia, hemoglobinuria, hematuria, proteinuria, hypertension, tachycardia, convulsions and coma. When a congenital deficiency in the homeostatic mechanism for copper exists, the metal accumulates in the liver, discrete areas of the brain, the cornea of the eye and other tissues, causing Wilson's disease. A wide variety of clinical disorders have been associated with a dietary deficiency of copper which respond to copper therapy.
They include anemia, depressed growth, nose disorders, depigmentation of hair or wool, abnormal wool growth, neo-natal ataxia, impaired reproductive performance, heart failure and gastro-intestinal disturbances.

Apart from the biological utility of copper, it also finds several applications in industries. It is used in the electrical industry as fine wires, computer bars and high conductivity tubes. It is also used in pipe making, roof sheeting, bronze paints and insecticides. In addition to this, it is an important pollutant in the environment resulting from the industrial discharge in the form of particulate or soluble copper waste from electroplating, chemical and textile industries. As a pollutant, copper have particular concern, because of the high degree of toxicity to aquatic organisms. In view of this, several analytical techniques have been reported for the determination of copper in various environmental importances.

Generally copper is widely distributed in environment, in the form of food material and animal origins and more over it is exist in +2 oxidation state in several compounds. It plays important role in carbohydrates and lipid metabolism, due to this reason it is fact that many of the higher plants and animal life needs the trace amounts of copper as nutrient to survive. Copper has 29 distinct isotopes ranging from the atomic mass number 52 to 80. Among this $^{63}\text{Cu}$, and $^{65}\text{Cu}$ are stable and naturally occurring isotopes of copper, remaining are radioactive isotopes. It also functions as a co-factor in various enzymes and in copper based pigments.

Lemos et al.$^1$ reported a new preconcentration and separation cloud point extraction technique for the determination of copper using 2-[2-methyl-benzothiazolylazo]-4-bromophenol (Me-BTBr) as an analytical complexing agent in
the presence of surfactant, triton X-114 by flame atomic absorption spectrometry in water samples. Shemirani\textsuperscript{2} describes the determination of trace amounts of lead and copper in water samples based on the cloud point extraction (CPE) technique prior to flame atomic absorption spectrometry using pyrogallol as complexing agent in the presence of triton X-114 as surfactant. Park et al.\textsuperscript{3} reported the spectrophotometric method for the determination of copper after selective extraction with (2-benzinidazolyl)c\textsuperscript{11}-c\textsuperscript{11}-(N-5-nitro-2-pyridyl hydrozone)-toluene as new complexing agent in the presence of Brij 58 in various milk samples having Beer’s law concentration range up to 2.5 \(\mu\text{g ml.\textsuperscript{-1}}\). Brasil et al.\textsuperscript{4} explained the factorial design for optimization of flow injection preconcentration procedure for copper (II) determination in natural waters using 2-aminomethylpyridine grafted silica gel as absorbent by spectrophotometric method in the recovery range of 95.2\% to 104\%.

Bekir\textsuperscript{5} reported the determination of copper in edible oils by atomic absorption spectrometric method after lead piperrazinedithiocarbamate solid-phase extraction. Reddy et al.\textsuperscript{6} reported a rapid sensitive extractive spectrophotometric method for the determination of copper(II) in pharmaceutical and environmental samples using benzyl dithiosemicarbazone as an analytical reagent forming yellowish complex in chloroform extract having maximum absorbance in concentration range of 0.5-0.4 \(\mu\text{g cm.\textsuperscript{-1}}\). Dalman and Karabocek\textsuperscript{7} reported a simple, selective solid-phase extraction procedure of copper (II) by modified octadecyl silica membrane disks with 2-{2-[2-hydroxyimino-1-methyl-propyl-deneamino]-ethylamino}-ethyl-imino}butan-2-one oxime in water and certified reference samples under optimized experimental conditions. Mahajan et al.\textsuperscript{8} prepared a new complexing
agent, cyclopentanone thiosemicarbazone for the determination of copper in biological samples by adsorption stripping voltammetry method using hanging mercury drop electrode in the concentration range of $3.14 \times 10^{-9} \text{M}$ to $1.57 \times 10^{-6} \text{M}$ with detection limit of $1.57 \times 10^{-9} \text{M}$. Lee and Choi\textsuperscript{9} established the column separation–preconcentration technique for the determination of copper with 1-nitroso-naphtho complex absorbed into activated carbon in stream water, ground water and diluted brass samples prior to AAS. A novel voltammetry method was described by Xia et al.\textsuperscript{10} for direct determination of copper in complex environmental samples based on the porous disorganized monolayer formed on the surface of the gold electrode by the self–assembly of mercapto acetic acid (MAA) technique. Tautkus\textsuperscript{11} reported a simple method for the determination of Cu in different tea sample by flame atomic absorption spectrometry under optimum conditions. Kim and Choi\textsuperscript{12} reported a flame atomic absorption spectrometric method for the determination of traces of copper based on preconcentration and adsorption of 1-nitroso-2-napthol complex on microcrystalline benzophenone in real samples. Anzano et al.\textsuperscript{13} explained the determination of copper at trace levels in solid samples of animal feed for direct analysis by electrothermal atomic absorption spectrometry in the concentration range of 10 $\mu \text{g/g}$. Bradshaw and Sellary\textsuperscript{14} reported a comparison study stripping potentiometry (CSP) in mercury and gold films at pH 4.5. Jankiwicz et al.\textsuperscript{15} reported the extractive spectrophotometric determination of copper (II) in soil samples forming complex with sodium(I) diethyl dithiocarbamate. Taher and Puri\textsuperscript{16} explained the differential pulse polarographic determination of copper in alloys and biological samples after preconcentration with 2-nitroso-1-napthol-4-sulphonic acid.
tetradecyldimethyl benzyammonium naphthalene adsorbent in the concentration range 0.7-28.0 \( \mu g/mL \) with correlation coefficient 0.9994 and RSD±0.88%. Solid phase spectrophotometric determination of copper was reported by Richter et al.\textsuperscript{17} in water samples using immobilized zincon in sephadex A25 resin at maximum absorbance 621.5 nm in the concentration range of 0.4 -300 ng/mL with detection limit of 0.12 ng/mL. Yamini et al.\textsuperscript{18} described the solid phase extraction of trace amount of copper with cupron on octadecyl silica cartridge and it's determination with atomic absorption spectrometry in natural water samples. Locatelli and Torsi\textsuperscript{19} established the voltammetric determination of metals in copper alloys at trace and ultra trace concentration and in standard reference materials NIST-SRM 1115, gunmetal BCS-CRM 207/2 and high, tensile brass BCS-CRM 390.

Ensafi and Abbasi\textsuperscript{20} reported the highly selective-cathodic stripping voltammetric determination of copper incorporating a benzylmonoxime and the complex adsorbed on to the hanging mercury drop electrode (HMDE) and the method was applied to the determination of copper in some commercial salts and river water at ppm concentration. Tarley et al.\textsuperscript{21} established the factorial design and doehlert matrix in optimization of flow system for preconcentration of copper on polyurethane foam loaded with 4-(2-pyridylazo)-resorcinol prior to flame atomic absorption spectrometry (FAAS) in water samples (mineral and tap water) and high salt aqueous (physiological serum) in the recovery range of 91.0% to 101.1%. Lemos et al.\textsuperscript{22} reported an on line solid phase extraction procedure for preconcentration and determination of copper in food samples using polyurethane foam loaded with Me-BTANC, packed in a minicolumn which was used as sorbent and absorbance of
the complex was read at 550nm by spectrophotometrically in dried shrimp samples in the recovery range of 91-108%. Castro Martha and Nivaldo explained the application of factorial design in optimization of preconcentration procedure for copper determination in soft drinks by flame atomic absorption spectrometry.

Dos Santos Walter et al. reported the determination of copper in powdered chocolate samples by slurry sampling prior to flame atomic absorption spectrometry with detection limit of 0.4 μg/g in comparison of reference material NIST SRM 158 rice flour and NIES CRM 10-rice flour. Yamini et al. described a novel sensitive solid phase extraction procedure and simultaneously developed the spectrophotometric determination of trace amounts of copper as it’s neocuprione complex and iron as it’s bathophenanthraoline complex using octadecyl silica cartridges in river, tap and well water samples. Budziak et al. explained the application of Nb205-SiO2 in preconcentration and determination of copper and cadmium by flow system with flame atomic absorption spectrometry in water samples.

Lee and Choi reported the spectrophotometric determination of copper and cadmium with ammonium pyrrolidinedithiocarbamate in nonionic tween 80 micellar media with the detection limits of 0.0493 μg ml⁻¹, 0.0393 μg ml⁻¹ respectively in real samples. Richtera et al. described the determination of arsenic and copper in environmental matrixes like river water, river sediments and soil samples using inductively coupled plasma-optical emission spectrometer (ICP-OES). Ferreira et al. reported the separation, preconcentration and sequential determination of trace
amounts of copper and zinc in natural water samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES) based on the complexation of copper(II), zinc(II) ions with 1-(2-thiazolylazo)-2-naphthol (TAN). Shokrollahi et al. proposed cloud point extraction procedure for the preconcentration of copper analysed by flame atomic absorption spectrometry in various samples using 4-hydroxy-2-mercapto-6-propylpyrimidine (PTU) as complexation reagent in environmental samples. Mohammad Ali Taher reported a determination of trace copper in biological and environmental samples by third derivative spectrophotometry after pre-concentration with the ion pair of nitroso-R and tetradecyldimethylbenzylammonium chloride on microcrystalline naphthalene. Xia et al. described the voltammetric method for the direct determination of copper in complex environmental samples using mercaptoacetic acid. Taher described a method for the determination of trace copper in biological and environmental samples by third derivative spectrophotometry after pre-concentration with the ion pair of nitroso-R and tetradecyldimethylbenzylammonium chloride on microcrystalline naphthalene.

Faquim and Munita reported the determination of copper by isotopic dilution employing substoichiometric extraction with dithizone in carbon tetrachloride reference materials, wheat flour, wine, and beer. Tehrani et al. described the determination of copper by flame atomic absorption spectrometry after preconcentration with activated carbon impregnated with a new schiff base in different water samples. Jadid and Eskandari reported preconcentration of copper with solid phase extraction and its determination by flame atomic absorption spectrometry in water samples having detection limit was in the range 2.26 µg/l.
Taher et al.\textsuperscript{37} designed a differential pulse polarographic determination of copper in alloys and biological samples after preconcentration with 2-nitroso-1-naphthol-4-sulphonic acid-tetradecyldimethylbenzylammonium-naphthalene adsorbent. Sturgeon et al.\textsuperscript{38} reported determination of copper in environmental matrices following vapor generation by conventional gas-liquid separator and directed via a stream of Ar carrier gas to an inductively coupled plasma atomic emission detection system. Shishehborea et al.\textsuperscript{39} described a spectrophotometric determination of trace copper after preconcentration with 1,5- diphenylcarbazone on microcrystalline naphthalene water samples and standard alloys.
Results

The present method successfully applied for the determination of copper in biological samples, plant materials and pharmaceutical preparations using simple chloroform extractive procedure prior to differential pulse polarography technique using newly synthesised analytical reagent 4-(2-hydroxy phenyl ethaminodiol) benzene-1,3-diol (4-2-HPEDB-1,3,D) and results were summarized in the Table IVA.1. The results obtained from the proposed method shows good agreement with reported method which already exist in the literature. The investigation of foreign ions was also studied and results were presented in the Table IVA.2 which made the method more sensitive and selective. The Table IVA.3 gives the information about the comparison of reagent, other electroanalytical techniques, concentration and samples of reported methods for the determination of copper with proposed method which shows the sensitivity and selectivity of the proposed method. The accuracy and precision of the proposed method was checked by the analysis of Certified Reference Materials (CRM’s) which is distributed by the National Institute of Standard Technology (NIST) and the results were shown in the experimental chapter II under section of samples analysis.
Discussions

Differential pulse polarographic studies

Effect of pulse amplitude and scan rate

The influence of the pulse amplitude was investigated. The results suggested that the increase in pulse amplitude leads the increase in sensitivity but also decrease in resolution, so maximum DPP peak current was obtained when the pulse amplitude was 50 mV. As for the scan rate; the current response with increasing the scan rate of 12 mVs\(^{-1}\) gave the maximum response. Accordingly, the optimum conditions for recording a maximum developed and sharper DPP peak was obtained at 12 mVs\(^{-1}\) for 0.05 mM [Cu-(4-2-HPEDB-1,3,D)]. The polarogramm of copper is shown in Fig II.15. Therefore scan rate : 12 mVs\(^{-1}\) and pulse amplitude 50 mV used in the present investigation.

Effect of pH

The effect of pH was investigated on the peak potential \(E_p\) and current intensity \(i_p\), using differential pulse polarography for [Cu-(4-2-HPEDB-1,3,D)] complex which is extracted from chloroform. The pH was varied in the range of 2.0 to 10.0 for [Cu-(4-2-HPEDB-1,3,D)] using various buffer solutions. The maximum peak current was obtained with pH 4.0 at peak potential – 420.0 mV when the pH has been increased from 2.0 to 10.0 the peak potentials have been shifted towards more negative values and it indicates proton participation in the reduction process at electrodes and the results were shown in Fig II.16. Therefore an acetate buffer of pH 4.0 is suitable for determination of copper for better sensitivity and selectivity.
Effect of 4-(2-hydroxy phenyl ethaminodiol) benzene-1,3-diol (4-2-HPEDB-1,3,D) concentration

The effect of concentration of 4-(2-hydroxy phenyl ethaminodiol) benzene-1,3-diol on the peak height was investigated at pH 4.0 ± 0.2 by using 100 μg/mL Cu(II) solutions. The concentration was varied in the range 0.01 mM to 1.0 M. Complete complex formation was obtained at a concentration of 0.1 mM of reagent for lower concentration level of Cu(II) solution. Therefore 0.1 mM reagent was used for the further investigation.

Effect of solvent

The extraction of [Cu-(4-2-HPEDB-1,3,D)] complex was carried out with different organic solvents such as dimethyl formamide, CCl₄, cyclohexane, chloroform, xylene, toluene, n-butanol, 1-pentanol, 1-amyl alcohol and nitrobenzene. Among these solvents the extraction of [Cu-(4-2-HPEDB-1,3,D)] complex efficiency more in chloroform when compare to other organic solvents. Therefore chloroform is chosen as solvent for extraction of [Cu-(4-2-HPEDB-1,3,D)] complex for further studies.

Calibration

The detection limit and the relative standard deviation values were obtained as 0.45 μg/mL, 5.45% respectively. The linearity is maintained in the concentration range of 0.05 to 200μg/mL for copper and calibration curve was constructed based on the general procedure and the graphically represented in Fig II.17. The correlation coefficient of proposed method was found as 0.9997 calculated using the formula $\frac{3sd}{m}$ where sd is standard deviation and m is the slope of the calibration curve.
Stoichiometry of the complex

The composition of the complex was found to be 1:1 = Cu$^{2+}$: 4-2-HPEDB-1,3,D. The stoichiometry of the complex was verified by analysis of Mole ratio method and Job’s method of continuous variation procedure and their data was shown in Fig II.18 and II.19.

Effect of foreign ions

The effect of interfering ions on the determination of copper in biological samples, plant material and pharmaceutical preparations was investigated, which is individually added to the copper having appropriate concentration and the general procedure was applied. The tolerable limits of various foreign ions are masked using suitable masking agents and recovery ranges (<2%) are shown in Table VIA.2. The results are almost quantitative in the presence of interfering ions to evaluate the feasibility and sensitivity of the present method.

Application

The present method was successfully applied for the determination of copper by simple chloroform extraction procedure prior to differential pulse polarography in biological samples, plant materials and pharmaceutical preparations and the results were shown in Table IVA1.

Conclusions

The present method was successfully applied for the determination of copper in biological samples, plant materials and pharmaceutical preparations. The differential pulse polarographic method, after chloroform extraction procedure, for the assay of
the copper using newly synthesized novel analytical reagent was reported and the results were compared with reference method with good agreement. The method has added advantages over reported methods i.e.

1. The newly synthesised organic reagent was less expensive, economical and it was synthesised at ordinary laboratory atmospheric conditions and very distinct in terms of selectivity, sensitivity towards metal ions.

2. Electrodes used in the present work for the analysis of copper in various samples are very sensitive and selective.

3. Statistical analysis and eliminating of time taking process, lengthy extraction steps makes the methods more sensitive and selective one for the determination of copper in biological samples, plant materials and pharmaceutical preparations.

4. The validity of proposed method was checked by standard reference material (SRM) tomato leaves 1573a which is provided by National Institute of Standard and Technology which show the high accuracy and precision of the proposed method.
Table IVA.1. Determination of copper in pharmaceutical preparations, biological samples and plant materials

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Samples</th>
<th>Present method</th>
<th>Reported method [40]</th>
<th>R.S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pharmaceutical preparations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Supradyn</td>
<td>0.865</td>
<td>0.86</td>
<td>0.35</td>
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<td></td>
<td>Certified value(0.86)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Multivitamin</td>
<td>0.27</td>
<td>0.26</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Iron minerals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Certified value(0.25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Human hair</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>46.52</td>
<td>45.11</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>69.12</td>
<td>68.98</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>63.99</td>
<td>61.81</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>Plant material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cabbage</td>
<td>38.75</td>
<td>37.66</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Banana</td>
<td>16.05</td>
<td>14.11</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Table IVA.2. Effect of Foreign ions in the determination of copper

<table>
<thead>
<tr>
<th>S.No</th>
<th>Ions</th>
<th>Concentration µg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SCN⁻, C₂O₄²⁻, Cd²⁺, Mg²⁺, Cr³⁺</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>Zn²⁺, Tartarate ion</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Al³⁺, Fe³⁺, CN⁻</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Co²⁺, Ni²⁺, NO₃⁻, Pb³⁺</td>
<td>10</td>
</tr>
</tbody>
</table>

*It can be masked by using 2mL of 2% sulphuric acid.*
Table IV A. 3. Comparison of the reagents for the determination of copper with other electro analytical techniques

<table>
<thead>
<tr>
<th>S.No</th>
<th>Reagents</th>
<th>Electroanalytical technique</th>
<th>Concentration</th>
<th>Samples</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Mercapto acid</td>
<td>Voltammetry</td>
<td>8×10⁻⁷ to 1×10⁻³ mol/L</td>
<td>Real environmental samples</td>
<td>[41]</td>
</tr>
<tr>
<td>2.</td>
<td>1-(2-thiazolylazo)-2-naphthol</td>
<td>Differential pulse polarography</td>
<td>0.18–13.5 and 0.30-17.3</td>
<td>Various samples</td>
<td>[42]</td>
</tr>
<tr>
<td>3.</td>
<td>crown ethers</td>
<td>Voltammetry</td>
<td>up to 100 ppb</td>
<td>Alcoholic beverages</td>
<td>[43]</td>
</tr>
<tr>
<td>4.</td>
<td>SSA</td>
<td>Adsorptive stripping voltammetry</td>
<td>3 – 23 μg L⁻¹</td>
<td>Crude oil, crude oil tank button sludge</td>
<td>[44]</td>
</tr>
<tr>
<td>5.</td>
<td>Nitroso-R dopant anion</td>
<td>Anodic stripping voltammetry</td>
<td>1.2 to 243.9 ng mL⁻¹</td>
<td>Water and human hair samples</td>
<td>[45]</td>
</tr>
<tr>
<td>6.</td>
<td>-</td>
<td>Anodic stripping voltammetry</td>
<td>100 to 300 mg</td>
<td>Beer</td>
<td>[46]</td>
</tr>
<tr>
<td>7.</td>
<td>Alizarin red S (ARS)</td>
<td>Catalytic-adsortptive stripping voltammetry</td>
<td>1.7×10⁻³ mol/L</td>
<td>Real samples</td>
<td>[47]</td>
</tr>
<tr>
<td>8.</td>
<td>4-2-HPEDB-1,3,D</td>
<td>Extractive differential pulse polarography</td>
<td>0.05 to 200 μg/mL</td>
<td>Biological samples, pharmaceutical and plant material</td>
<td>Present method</td>
</tr>
</tbody>
</table>
REFERENCES


34. E. S. Faquim and C. S. Munita, Biological Trace Element Research, 43(1) (1994) 669.


Introduction

Nickel is a silvery white hard and ductile metal. It is a fairly good conductor of heat and electricity. The most common oxidation state of nickel is +2 and $\text{Ni}^{\text{+2}}$ is the stable nuclide of the existing element. It is an ancient metal used in preparation of alloys, rechargeable batteries, catalyst and other chemicals, coinage and plating, many industrial and consumer products.

Nickel plays numerous roles in biology. Nickel is the metal component of enzyme urease which assist in the hydrolysis of urea and as considered to be essential to plants and domestic animals. Nickel obtained mostly in the form of ore deposits like limestone and garnilite. Based on the geophysical survey says that nickel on the earth is postulated to be concentrated in the earth's core. Generally nickel compounds occur in the environment at low levels. Human exposed to nickel by treating air, drinking water, eating food or smoking cigarette, contaminant soil or water may also result in nickel exposure, due to this, several disorders will be occur like different types of cancer, respiratory failure, asthma and chronic bronchitis. Nickel sulfide fumes and dust is carcinogenic and carbonyl compounds are an extremely toxic gas which is responsible for release of nickel into environment.

Bijoli Kanti Pal\(^1\) reported a rapid quenchofluorimetric determination of nickel(II) in some real and environmental samples using 4,7-diphenyl 1,10-phenanthrolinedisulfonate as chelating reagent. Hanwen Sun and Ran Suo\(^2\) reported the determination of ultra-trace amounts of nickel in environmental samples by
atomic absorption spectrometry with in-situ trapping of volatile species in an iridium-palladium coated graphite furnace. Qiufen Hu et al. described a study on solid phase extraction and spectrophotometric determination of nickel in waters and biological samples using QADMAA. Harun Cftc et al. reported the determination of nickel in some plants with reversed-phase high performance liquid chromatography (HPLC) in thyme, nettle, tobacco, radish and lime. Lars Fu et al. proposed a speciation of nickel in airborne particulate matter by means of sequential extraction in a micro flow system and determination by graphite furnace atomic absorption spectrometry and inductively coupled plasma mass spectrometry. Atomic absorption spectrometric determination of trace amounts of nickel was reported by Tahar et al. after preconcentration with [1-(2-pyridylazo)-2-naphthol]-naphthalene adsorbent or after adsorption of its complex on microcrystalline naphthalene.

Teissedre et al. studied the determination of nickel in french wines and grapes and traces possible sources of contamination in wine using graphite furnace atomic absorption spectrometry. Cano Pavon et al. described the determination of nickel in biological samples by electrothermal atomization-atomic absorption spectrometry involving a prior extraction with 1,5-bis (di-2-Pyridylmethylene) thiocarbono-hydrazide. Amini et al. studied the determination of trace amounts of nickel by differential pulse adsorptive cathodic stripping voltammetry using calconcarboxylic acid as a chelating agent in chocolate sample. Sitki Baytak et al. reported the determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA in standard reference tea leaves sample (GBW-07605) and the results
demonstrated good agreement with the certified values. Zhimei Sun et al.\textsuperscript{11} illustrated the determination of trace nickel in water samples by cloud point extraction, preconcentration coupled with graphite furnace atomic absorption spectrometry using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP). Kiyohisa Ohta et al.\textsuperscript{12} reported the determination of nickel in water by electrothermal atomic absorption spectrometry with preconcentration on a tungsten foil.

Ershovan and Ivanov\textsuperscript{13} developed the of direct determination of trace nickel in environmental samples by diffuse reflection spectroscopy using chromaticity characteristics in soil samples. Luo et al.\textsuperscript{14} reported a spectrophotometric determination of trace nickel in environmental samples by p-acetyl arsenazo. Kalyakina et al.\textsuperscript{15} described the sorption preconcentration and determination of nickel in wastes of heat power industry by diffuse reflection spectroscopy using 1-(2-pyridilazo)-2-naphtol (PAN). Tautkus et al.\textsuperscript{16} proposed a extractive preconcentration and determination of nickel in water and waste water samples by atomic absorption spectrometry. Burguera et al.\textsuperscript{17} described the determination of nickel in saliva by electrothermal atomic absorption spectrometry using various chemical modifiers with Zeeman-effect background correction.

Chamon et al.\textsuperscript{18} described a speciation analysis of nickel in the soils of tejgaon industrial area of Bangladesh. Pourreza et al.\textsuperscript{19} proposed solid phase extraction of nickel as methylthymol blue complex on naphthalene adsorbent by flame atomic absorption spectrometric determination in ore and water samples. Walter et al.\textsuperscript{20} studied the field sampling system for determination of cadmium and nickel in fresh
water by flame atomic absorption spectrometry. Muddukrishna et al.\textsuperscript{21} developed a sensitive method for the determination of nickel in environmental samples with X-ray fluorescence spectrophotometry. Eskandari and Kamali\textsuperscript{22} described H-point standard method for the selective simultaneous determination of nickel and copper using 1-(2-pyridylazo)-2-naphthol (PAN) in tween 80 micellar media at 548 and 579 nm respectively in water and alloy samples in ppm range. Suresh et al.\textsuperscript{23} employed the voltammetry method for the determination of nickel in water and soil samples.

Minami et al.\textsuperscript{24} reported a method for the determination of cobalt and nickel using graphite furnace atomic absorption spectrometry after co-precipitation with scandium hydroxide at pH 8.0 to 10.5 in river water sample. Determination of nickel in environmental samples with inductively coupled plasma atomic emission spectroscopy was described by Ren et al.\textsuperscript{25} Giannetto et al.\textsuperscript{26} developed an electroanalytical method to analyse Pb, Cu, Cd and Ni in particulate matter 2.5 (P.M) and nickel is determined by differential pulse adsorptive cathodic stripping voltammetry. Yang et al.\textsuperscript{27} reported the simple and sensitive spectroscopic method for the determination of nickel in steel and aluminum alloy samples using 5-(6-bromo-2-benzothiazoylazo)-8-hydroxy quinoline reagent. The furfural-2-benzothiazoyl hydrazone employed as chromogenic reagent for determination of nickel by spectrophotometry was reported by Odashima and Tossidis\textsuperscript{28}. Diagomanolin et al.\textsuperscript{29} reported the determination of Ni, Cr, Cu in karoon river samples in Iran by graphite furnace atomic absorption spectrophotometry with the detection limit of ppm level. Sun et al.\textsuperscript{30} described the determination of trace nickel in water sample by cloud point extraction of preconcentration coupled with graphite furnace atomic absorption spectrometry.
Burguera et al.\textsuperscript{31} reported the electrothermal atomic absorption spectrometry using various chemical modifier with Zeeman-effect background correction for the determination of nickel in saliva with detection limit of 0.11 µg/mL in seronorm blood serum standard reference material. Yao et al.\textsuperscript{32} described the solid-phase extraction of nickel from electrolytic manganese using a sorbent by syringe technique by electrothermal atomic absorption spectrometry in standard reference material AME 2003 in the recovery range of 98.3-103.5%. Afzali et al.\textsuperscript{33} developed the flame atomic absorption method for the determination of trace amounts of nickel after extraction and preconcentration on to naturally modified analcime zeolite loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol with detection limit of 20 µg/mL in various standard reference material. Pal et al.\textsuperscript{34} explained fluorimetric method for the determination of Ni in ultra trace levels using 1,10-phenanthroline disulfonate having \( \lambda_{\text{max}} \) at 444.8 nm in concentration of 1 ng/mL in real and environmental samples.
Results

The extractive chloroform procedure was used for the determination of nickel prior to differential pulse polarography using a novel analytical reagent 4-(2-hydroxy phenyl ethaminodiol) benzene-1,3-diol (4-2-HPEDB-1,3,D) in biological samples, plant materials and pharmaceutical preparations and their analytical data was incorporated in the Table IVB.1 to IVB.3. The proposed method was validated by the analysis of Certified Reference Materials (CRM's) and gives the precision and accuracy of the present method and results were shown in Table IVB.4. The investigation of interfering ions for the determination of nickel was carried out and the results were summarized in the Table IVB.5. The analytical data obtained from the above said method satisfactory and compared with reported method which exists in the literature shows that there is no significant difference between reported and proposed methods. A comparison of few analytical parameters such as concentration range, reagent, solvent media, limit of detection and techniques for the determination of nickel with other reported methods exist in literature and their information is presented in Table IVB.6.
Discussions

Differential pulse polarographic studies

Effect of pH

The effect of pH was investigated on the peak potential $E_p$ and current intensity $i_p$ at -630.0 mV for Ni (II) which is shown in Fig II.20 at different concentrations because it is an important analytical parameter shows the significant effect for [Ni-(4-2-HPEDB-1,3,D)] complex. The pH of acetate buffer was taken in the range of 3.0-7.0 and the peak height measured for each concentration level of Ni (II). At all concentration levels of Ni (II) maximum peak height was found between 3.5 to 4.5. Therefore, the acetate buffer of pH 4.0 was chosen optimum pH for throughout the experiment and the results were represented graphically in Fig II.21.

Effect of pulse amplitude and scan rate

The influence of the pulse amplitude was investigated for the determination of nickel by differential pulse polarography after simple chloroform extraction procedure. The results suggested that peak current reached the maximum value when the pulse amplitude was 50 mV. As for the scan rate, the current response with increasing the scan rate of 12 mVs$^{-1}$ gave the maximum response. Hence scan rate 12 mVs$^{-1}$ and pulse amplitude 50 mV was selected for further analysis under the optimum conditions for recording a maximum developed and sharper DPP peak for 0.5 mM [Ni-(4-2-HPEDB-1,3,D)] complex.
Effect of reagent concentration

The effect of reagent concentration was play an important role in the preconcentrate the metal ion. The reagent concentration was studied by taking the concentration range of 0.01mM to 0.1mM. The chelating concentration increased up to certain values, which were sufficient for total complexation. Therefore concentration of 0.1mM is suitable for reaching the near quantitative extraction efficiency.

Choice of solvent

The extraction of \([\text{Ni-(4-2-HPEDB-1,3,D)}]\) complex was carried out with different organic solvents like dimethyl formalmide, CCl\(_4\), cyclohexane, chloroform, xylene, toluene, n-butanol, 1-pentanol, 1-amy alcohol and nitrobenzene. Among these solvents the extraction of \([\text{Ni-(4-2-HPEDB-1,3,D)}]\) complex efficiency more in chloroform when compare to other organic solvents. Therefore chloroform is chosen as solvent for extraction of \([\text{Ni-(4-2-HPEDB-1,3,D)}]\) complex for further studies.

Calibration, detection limit and precision

The calibration curve was constructed based on the general procedure under the optimised conditions at the concentration range of 0.05-200 \(\mu g/mL\) with correlation coefficient as 0.9998. The detection limit was found to be 0.052 \(\mu g/mL\) in the final solution by taking six individual replicates of nickel solution which gives the relative standard deviation as 5.35% and it's relative typical curve was shown in Fig.II.22.
Stoichiometry of the complex

The composition of the complex was determined by Mole ratio method and Job's continuous variation method and ratio of the nickel with 4-2-HPEDB-1,3,D was confirmed as 1:1 (Ni$: 4-2$-HPEDB-1,3,D). It is represented graphical manner which is shown in Fig II.23 and II.24.

Application

Determination of nickel by differential pulse polarography after chloroform extraction method was successfully applied in biological samples, plant materials and pharmaceutical preparations and the results were shown in Table IVB1 to IVB4.

Effect of Foreign ions

The selectivity of the proposed method was enhanced by the study of the diverse ions for the determination of nickel in biological samples, plant material and pharmaceutical preparations and the results were shown in the Table IVB.5. Many of the diverse ions were tolerated up to maximum level by using suitable masking agents with causing error of >2% during the analysis of nickel ion. The results are almost all quantitative in the presence of diverse ions to elevate the feasibility and selectivity of the proposed method at appropriate amount of nickel solution followed by the general procedure.

Conclusion

In present work monitoring of nickel in biological samples, plant materials and pharmaceutical preparations was analyzed by the differential pulse polarography after a simple chloroform extraction procedure. For this purpose a new analytical
reagent was synthesised for the metal complexation and the results were compared with reported method with good agreement. This method have additional advantages over reported method such as

1. The proposed method is an alternative method for the determination of nickel in biological samples, plant materials and pharmaceutical preparations comparison with other analytical techniques which is present in Table IVB.6 in terms of their detection limits and concentration range or their values 0.15 µg/mL, 0.05-200 µg/mL respectively of proposed method shows the sensitivity of the method.

2. The analytical reagent 4-(2-hydroxy phenyl ethaminodiol) benzene-1,3-diol synthesised for the metal complexation was distinct in view of sensitivity and selectivity.

3. The extraction of metal complex from organic solvent is owing to the low dielectric constant and polarisable compound of the organic phase.

4. The study of diverse ions like cations, anions and other salts enhance the sensitivity and feasibility of the proposed method.

5. Avoidance of tedious and time consuming process made the method more sensitive and selective for the determination of metal ion in the samples because electroanalytical techniques are more rapid and simple.

6. The method validation was done by the analysis of Standard Reference Materials (SRM's) distributed by National Institute of Standard Technology [NIST (USA)] which shows the precision and accuracy of the method.
### Table IVB.1. Determination of nickel in biological samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified values</th>
<th>Spectrophotometry [1]</th>
<th>Present method (n=5)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIES No.5 Human hair: Pb(6.0), Cd(0.20), Sb(0.07), Zn(169), Al(240), Sc(0.05), Fe(225), Mg(208), Hg(4.4), Co(0.10), Rb(0.19), K(34), Mn(5.2), Cu(16.3), Ti(22), Ca(728), Cr(1.4), Ba(2.2), Se(1.4), Na(26), Sr(2.3).</td>
<td>1.80</td>
<td>1.90 ± 0.12</td>
<td>1.965±0.65</td>
</tr>
</tbody>
</table>

bMean values for five determinations

### Table IVB 2. Determination of nickel in plant materials

<table>
<thead>
<tr>
<th>Samplesa</th>
<th>AAS method [35]</th>
<th>Present method (n=5)f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pisum sativum (Hulls)</td>
<td>2.060 ± 0.003</td>
<td>2.065±0.068</td>
</tr>
<tr>
<td>Mangifera indica leaves</td>
<td>2.150 ± 0.004</td>
<td>2.153±0.072</td>
</tr>
<tr>
<td>Eucalyptus leaves</td>
<td>1.038 ± 0.002</td>
<td>1.044±0.013</td>
</tr>
<tr>
<td>Azadirachta indica leaves</td>
<td>1.481 ± 0.005</td>
<td>1.489±0.015</td>
</tr>
</tbody>
</table>

aSamples collected from Acharya N.G.Ranga Agricultural college, Tirupati, Andhra Pradesh, India.
bMean values for five determinations
Table IVB.5. Tolerable limit of diverse ions on the determination of nickel with error of ±2%

<table>
<thead>
<tr>
<th>Diverse ions</th>
<th>Tolerable limit(^a) (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^+), Mg(^2+), NO(_3^-)</td>
<td>60,0000</td>
</tr>
<tr>
<td>Li(^+), Al(^3+), PO(_4^{3-}), NO(_3^-), ClO(_4^-), SO(_4^{2-})</td>
<td>40000</td>
</tr>
<tr>
<td>Ca(^2+), Sr(^2+), B(III), ClO(_3^-), BrO(_3^-), IO(_3^-)</td>
<td>30000</td>
</tr>
<tr>
<td>Mn(^2+), Fe(^3+), Ce(IV), Mo(VI), Br</td>
<td>20000</td>
</tr>
<tr>
<td>V(V), Ti(IV), Cr(VI), Bi(III), U(IV), Cr(VI), Ba(^2+)</td>
<td>3000</td>
</tr>
<tr>
<td>Cu(^2+), Pd(^2+), Zn(^2+), Cd(^2+), La(^3+), Cr(^3+), Cl(^-), Zr(IV)</td>
<td>1000</td>
</tr>
<tr>
<td>Pb(^2+), Bi(III), Hg(^2+), Ag(^+), Th(IV), Sb(^3+), Sn(IV),</td>
<td>500</td>
</tr>
<tr>
<td>Au(^3+), Te(IV), Se(IV),</td>
<td>300</td>
</tr>
<tr>
<td>Co(^2+)</td>
<td>150</td>
</tr>
</tbody>
</table>

\(^a\)Can be masked up to 3000 µg/mL by the addition of 2 mL of 2% sulfonic acid
Table IVB.6 Comparison of various reagents for the determination of nickel with other techniques

<table>
<thead>
<tr>
<th>S. No</th>
<th>Reagents</th>
<th>Solvent or medium</th>
<th>Techniques</th>
<th>Concentration range</th>
<th>Limit of detection</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-(2-Quinolyazo)-5-dimethylaminomiline QADMAA</td>
<td>sodium dodecyl sulfonate (SDS)</td>
<td>Spectrophotometry</td>
<td>0.01-0.6 μg/mL</td>
<td>0.2 μg/mL</td>
<td>[3]</td>
</tr>
<tr>
<td>2</td>
<td>2-pyridylazo 2-resorcinol (PAR)</td>
<td>acetate buffer</td>
<td>HPLC</td>
<td>Up to 50 μL</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>3</td>
<td>1-phenyl (3-methyl-3-benzoyl) 5-pyrazolone</td>
<td>surfactant Triton X-100</td>
<td>GFASS</td>
<td>Up to 100 ng/mL</td>
<td>0.12 ng/mL</td>
<td>[11]</td>
</tr>
<tr>
<td>4</td>
<td>1-pyridylazo(-2-naphthol) (PAN)</td>
<td>surfactant (Amberlite XAD-resin)</td>
<td>ICPAES</td>
<td>0.10-275 μg/L</td>
<td>0.20 μg/mL</td>
<td>[36]</td>
</tr>
<tr>
<td>5</td>
<td>2-(2-quinolyazo) dimethyl dimethylaminomiline(QADEAA)</td>
<td>sodium dodecyl sulfonate (SDS)</td>
<td>Spectrophotometry</td>
<td>0.01-0.4 μg/mL</td>
<td>0.2 μg/mL</td>
<td>[37]</td>
</tr>
<tr>
<td>6</td>
<td>4-(2-hydroxy phenyl ethaminodiol), benzene-1,3-diol</td>
<td>acetate buffer</td>
<td>Extractive differential pulse polarography</td>
<td>0.05-200 μg/mL</td>
<td>0.052 μg/mL</td>
<td>Present work</td>
</tr>
</tbody>
</table>
REFERENCES


