Chapter 5

Synthesis and Characterization of Cobalt Nitroprusside Nano Particles: Application to Sulfite Sensing in Food and Water Samples

5.1 Introduction

Polycyanide metal complexing reagents, with a general formula \([M(CN)_5L^n]^{n^-}\) where \(M=\text{Fe, Ru, Os}\) and \(L\) a variable ligand (\(\text{H}_2\text{O}, \text{CN}^-, \text{NH}_3, \text{amines, NO, NO}_2^-, \text{N-heterocyclic molecules, CO, etc.}\) has received much attention and systematic investigation of their electronic structure and reactivity are persuaded [1]. Pentacyanonitrosylferrate, \([\text{Fe(CN)}_5\text{NO}]^3^\) is also referred as nitroprusside (NP) is one of the important ligands of the above mentioned family because of its ability to complex with various transitional metal ions. Metal nitroprussides (MNP) have received great attention of the scientific community as electrochemical sensors recently due to its versatility and electrocatalytic activity [2–6]. MNP complexes where \(M=\text{Sn, Ni, Zn, Cd, Co, Pb etc.}\) were prepared as thin films on the surface of various electrodes using different strategies and successfully used for the quantification of wide range of analytes like ascorbic acid, hydrazine, L-cysteine, hydrogen peroxide, sulfide, sulfate etc [2, 3, 7–12]. In recent years carbon paste electrodes (CPE) have been extensively used over surface modified rigid electrodes for the determination of wide range of analytes due to their easy fabrication, wide potential window, easy surface renewability and low residual currents [13].

Nano scale sized metallic particles are attracting considerable attention for their intriguing properties and potential applications [14]. Recently, materials in the nanometer range have shown superior or advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical as well as biological sensors. Metal nanoparticles as catalysts have been vigorously investigated because of their specific properties such as large surface area and their superior properties which are different from their bulk counterparts [15]. Inorganic nanoparticles are very useful candidates for electrochemical studies owing to their outstanding activity and catalytic power [16–18]. The large surface-to-volume ratio and the active sites of these nano-sized metal particles in electrocatalysis constitute a part of the driving force in developing the nanosized electrocatalysts. The application of the carbon paste electrodes incorporating nanoparticles exhibited considerable improvement in the electrochemical behavior [19, 20]. The presence
of nanoparticles in electrochemical sensors can decrease the over potentials of many analytes. The analytical devices made with metal nanoparticles have attracted a remarkable interest to realize electrochemical sensors.

Sulfite is well known for its use in food and beverage industries as a preservative. Sulfite prevents oxidation, inhibits bacterial growth, enzyme activity causing browning and inhibits the growth of microorganisms during storage [21]. Despite these great advantages, the sulfite content in food and beverages should be strictly limited due to its potential toxicity and harmful effects towards hypersensitive people. Before 1986, sulfites were considered incorrectly harmless for consumers and they received the “Generally Recognized As Safe” (GRAS) status. In the same year US Food and Drug Administration (FDA) revoked the GRAS status and required sulfite declaration on the label of any food item containing 10 ppm levels of sulfite [22]. It is considered as one among the well known food allergens. Sulfite hypersensitivity is usually, but not exclusively, found within the chronic asthmatic population. Adverse reactions to sulfites in nonasthmatics are extremely rare. Asthmatics who are steroid-dependent or who have a higher degree of airway hyper reactivity may be at greater risk of experiencing a reaction to sulfite-containing foods. Even within this limited population, sulfite sensitivity reactions vary widely, ranging from no reaction to severe. These manifestations may include dermatological, respiratory or gastrointestinal symptoms [23, 24]. In order to quantify such trace level sulfite, there is a significant progress in its quantification technology. Several methods have been reported for the quantification of sulfite from a variety of sample matrices [21]. These methods are mainly based on techniques like electrochemical [25–33], biosensors [34], chromatography [35], chemiluminescence [36–38] and spectrophotometry [39]. Among these, electrochemical methods find widespread use due to their simplicity, easy modification and easy adaptability. Chemically modified electrodes (CMEs) have become significant ones in recent years due to their tailoring made properties which imparts selectivity as well as analyte specificity

M.H. Pouranghi-Azar et al. [40] have used the glassy carbon electrode electrochemically modified with CoNP complex to oxidize sulfite. A pioneering work on the synthesis of cyano-bridged coordination polymer nano objects like Prussian blue and its analogues have been reported in recent years [41, 42]. Different techniques such as reverse micelle, ionic liquid by using stabilizing ligands in solution have been developed to prepare metal
nanoparticles [43–45]. Very few reports appeared on the direct synthesis of Prussian blue analogue nanoparticles without any templating and/or additives [46, 47].

In most of the reported protocols, metal nitroprussides are electrochemically coated onto the rigid electrode surface and used as an electrochemical sensor. The surface renewal is quite cumbersome in all these rigid surface modified electrochemical sensors. In order to overcome the surface renewability problem of this kind of electrodes, an attempt has been made for the first time to synthesize CoNP nanoparticles in solution phase without any additives. Then the synthesized CoNP nano particles have been used as a modifier in designing an electrochemical sensor for the sulfite quantification. The proposed sensor has been successfully applied in the measurement of sulfite from a variety of food stuff and water samples.

5.2 Experiment
5.2.1 Apparatus
All the samples were characterized by X-ray diffraction (Bruker aXS Model D8 Advance powder X-ray diffractometer, Cu Kα source λ = 15.418 nm, θ–2θ geometry). IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (Diamond crystal ATR mode, resolution 4 cm⁻¹, 400–4000 cm⁻¹). Scanning electron micrographs were obtained using Quanta-200 scanning electron microscope by dispersing sample conducting carbon tape and sputter coating with gold to improve the conductivity. Cyclic voltammetry experiments were performed using CH Instruments electrochemical work station (model CHI 619B, CH Instruments, Texas, USA) in a standard three electrode cell. A carbon paste electrode as a working electrode, Pt wire as the counter electrode and Ag/AgCl served as the reference electrode.

5.2.2 Chemicals and reagents
Sodium sulfite (1000 ppm): Prepared by dissolving 0.157 g of Na₂SO₃ in 100 mL of water. Sulfite solutions of desired concentrations were obtained by diluting the stock solution.
Cobalt chloride (0.02 M): Prepared by dissolving 0.047 g of CoCl₂ 6H₂O in 10 mL water.
Sodium nitroprusside (0.01 M): Prepared by dissolving 0.0297 g of Na₂[Fe(CN)₅NO] 2H₂O in 10 mL water.
Potassium nitrate (0.5 M): Prepared by dissolving 5.055 g of potassium nitrate in 100 mL of acetate-acetic acid buffer solution of pH 5. All solutions were prepared using double distilled water.

5.2.3 Synthesis of Cobalt Pentacyanonitrosylferrate
CoNP was synthesized by precipitation protocol using three different procedures: Drop by drop, Sonication and bulk mixing methods at a temperature of 5–10°C.

Drop by drop (DbD) method: 10 mL aqueous solution of 0.01 M sodium nitroprusside was taken in a dropping funnel and it was added dropwise to 10 mL of 0.02 M aqueous solution of cobalt chloride taken in a beaker which was thermostated at 5–10°C under vigorous stirring. The solution turns turbid due to the formation of cobalt nitroprusside complex. It is referred as n-CoNP in all further studies.

Sonication method: 10 mL each of aqueous solutions of 0.01 M cobalt nitroprusside and 0.02 M cobalt chloride were mixed at 5–10°C and sonicated for 30 min. It is designated as s-CoNP.

Bulk mixing method: In this method, 10 mL of aqueous solutions of 0.01 M sodium nitroprusside and 0.02 M cobalt chloride which were maintained at 5–10°C were mixed immediately in a beaker. The resulting compound has been designated as b-CoNP.

In all the three cases, the pH of the solutions were maintained in acidic condition to avoid the formation of metal hydroxides and the resultant precipitates were left overnight without disturbing. After 24 hours, the supernatant liquids were decanted and the residues were centrifuged. The prepared CoNP compounds were initially washed with plenty of water then finally with alcohol. The residue was collected in a petridish and dried at room temperature. The resulted CoNP particles from all the three procedures were used as a modifier in fabricating carbon paste electrodes.

5.2.4 Electrode preparation
The carbon paste electrode was prepared manually by thoroughly mixing the dispersed graphite powder with n-CoNP at 15:1 mass ratio and subsequently adding 38% (w/w) of mineral oil. The resultant mixture was ground in an agate mortar for 10–15 min. The obtained paste was packed into a capillary tube from the wider end. A copper wire was inserted from the opposite end of the capillary to obtain the electrical contact. Similarly b-CoNP and s-CoNP modified CPE electrodes were prepared. Similarly bare CPE was also prepared using
graphite powder and mineral oil. All these electrodes were dried for 24 h at room temperature and the reisistivity was measured using a multimeter. The reisistivity was measured and it has been found to be 10–12 Ohms.

5.2.5 Sample preparation procedures
5.2.5.1 Sugar
Commercially available 25 grams of sugar sample was dissolved in distilled water and made up to 100 mL. One mL aliquot of diluted sugar solution was used for analysis.

5.2.5.2 Dry grapes
Ten grams of dried grapes were taken in a 250 mL beaker and soaked by adding 25 mL of 2 M NaOH solution. After 30 min. the grapes were smashed gently using glass rod then it was allowed to stand for 2 h. The contents in the beaker were thoroughly mixed and filtered quantitatively using whatman filter paper. The filtrate was neutralized by concentrated sulfuric acid and the pH was adjusted to 5 and the solution was made up to 100 mL. One mL of the diluted sample solution was used for the analysis.

5.2.5.3 Wine and water samples
White wine and water samples were also analyzed for sulfite content without any pretreatment. 0.5 and 1.0 mL volumes of wine and water samples were used for the analysis.

5.3 Results and Discussion
Cobalt nitroprusside complex has been synthesized from three different approaches. The complex resulted from all the three approaches has been characterized by IR spectroscopy to confirm the presence of functional groups. The SEM was used to understand the surface morphology and the difference in the grain size and by the XRD pattern to obtain the information about the phase purity. Carbon paste electrodes were prepared using all the three CNP complexes as indicator species to study their electrochemical behavior. Then the electrocatalytic activity of the n-CoNP, s-CoNP and b-CoNP to oxidize the sulfite has been compared using the modified CPEs. The n-CoNP modified CPE showed a better catalytic activity towards the oxidation of sulfite compared to other two CoNP modified CPEs. Scan rate studies have been carried out to understand the electrode process. Then optimization of electrolyte, pH and interference of various ions generally present in the food products have
been carried out. To check the applicability of the n-CoNP complex, sulfite has been quantified in various food samples using the CPE prepared using cobalt nitroprusside complex.

5.3.1 Surface morphology of cobalt nitroprusside particles
The morphology and grain sizes of the prepared CoNP particles were studied by recording the SEM images for all the three types. The surface morphology of cobalt nitroprusside particles were of almost same size for all the three types. However they have differed in grain sizes. Accordingly the particles of all the three types composed of well dispersed spheres. The n-CoNP contains very small particles, where as s-CoNP comprised of small particles and medium sized particles and more number of bigger particles can be seen in case of b-CoNP. The SEM images are shown in the Fig.5.1 (A–C, A’–C’) under two different magnifications.

5.3.2 IR study
The CoNP prepared by drop by drop, sonication and bulk mixing methods were characterized by FTIR spectroscopy (Fig.5.2). The sharp peak at 1617 cm\(^{-1}\) is due to the NO (nitrosyl) stretching vibration. However an intense peak at 2183 cm\(^{-1}\) can be related to the stretching

![FTIR Spectrum](image)

**Fig.5.2** FTIR spectrum of n-CoNP compound.
frequency of CN (cyanide) group. The broad band at 3376 cm\(^{-1}\) might be due to -OH (hydroxyl) group stretching vibration. The peaks assigned are in good agreement with the reported literature [48]. These studies revealed that the complex synthesized is a hydrated one.

### 5.3.3 XRD study

X-ray diffraction was used to identify the phase purity of synthesized CoNP complex. The XRD pattern of the as synthesized sample is shown in Fig.5.3. Sharp reflections were observed at d-spacing corresponding to the n-CoNP phase. The sharp reflections indicate that the as synthesized product is highly crystalline. Same kind of X-ray patterns (Bragg reflections in all

![XRD spectrum of n-CoNP compound.](image)

The samples were observed at same 2\(\Theta\) values) were obtained for s-CoNP and b-CoNP (data not shown). The average crystallite size of n-CoNP was calculated using the Scherrer formula and it has been found that the crystallite size varies within 53–55 nm. Obtained XRD pattern of the n-CoNP matches with the crystallographica pdf No. 80 - 2395.
5.3.4 Electrochemical behavior of cobalt nitroprusside modified carbon paste electrode

Cyclic voltammogram of CoNP CPE’s were recorded in the scan range between 0 and 1 V vs. Ag/AgCl electrode in 0.5 M KNO₃ as a supporting electrolyte at a scan rate of 0.5 Vs⁻¹ (Fig.5.4). The voltammograms exhibited a pair of peaks with a formal potential $E^\ddagger = (E_{pa} + E_{pc})/2$ of 0.48, 0.54, 0.53 V, respectively for n-CoNP, s-CoNP, b-CoNP compounds (Fig. 5.4). The peaks are well resolved and the ratio of the anodic to cathodic peak currents were found to be almost unity which indicates that the process is reversible and the peaks are due

![Graph showing cyclic voltammograms of CoNP-modified carbon paste electrodes](image)

**Fig.5.4** Overlaid cyclic voltammograms of CoNP-modified carbon paste electrodes in 0.5 M KNO₃.

to [Fe (II) (CN)₆NO]/ [Fe (III) (CN)₆NO] redox couple. The redox potentials of all the CoNP nanoparticles prepared by the three approaches were in good agreement with the literature [2].

The electrocatalytic activity of CoNP particles prepared by the three approaches was examined by studying the cyclic voltammetry in presence of sulfite. The cyclic voltammograms of the three CPE’s modified with n-CoNP, s-CoNP and b-CoNP in absence and in presence of 3.4 mM sulfite are shown in Fig.5.5 (A) to Fig.5.5 (C).
Fig. 5.5  (A) Overlaid cyclic voltammograms of n-CoNP modified CPE (a) in absence (b) in presence of 3.4 mM sulfite.

Fig. 5.5  (B) Overlaid cyclic voltammograms of s-CoNP modified CPE (a) in absence (b) in presence of 3.4 mM sulfite.
The electrochemical response i.e. increase in the anodic peak current due to electrocatalytic oxidation of sulfite was considerably greater in case of n-CoNP CPE compared to other two electrodes.

![Graph](image)

**Fig.5.5** (C) Overlaid cyclic voltammograms of b-CoNP modified CPE (a) in absence (b) in presence of 3.4 mM sulfite.

### 5.3.5 Electrocatalytic oxidation of sulfite at nano cobalt nitroprusside modified carbon paste electrode

In order to understand the electrocatalytic activity of n-CoNP CPE towards sulfite oxidation, the voltammetric behavior of the electrode in presence of sulfite was compared with that of the bare electrode. The Fig.5.6 illustrates the overlaid cyclic voltammograms of n-CoNP modified and bare carbon paste electrode in absence and in presence of 3.4 mM sulfite in 0.5 M KNO3 as an electrolyte. It is clear that the presence of CoNP nanoparticles as a modifier in the electrode significantly improves the anodic current of the modified electrode in presence of sulfite. These studies revealed that the modified electrode with n-CoNP spheres acts as an efficient electrocatalyst and improves the analytical performance of the electrode compared to bare electrode. The reaction between the sulfite and modifier molecule is a one electron transfer process and it follows heterogeneous EC catalytic mechanism [40].
KCo [Fe $^{II}$ (CN)$_3$NO] $\rightarrow$ Co [Fe $^{III}$ (CN)$_3$NO] + K$^+$ + e$^-$ (E)

$\uparrow$

k

$\downarrow$

Co [Fe $^{III}$ (CN)$_3$NO] + K$^+$ + HSO$_3^-$ $\rightarrow$ KCo [Fe $^{II}$ (CN)$_3$NO] + HSO$_3^-$ (C') slow

Co [Fe $^{III}$ (CN)$_3$NO] + K$^+$ + HSO$_3^-$ + H$_2$O $\rightarrow$ KCo [Fe $^{II}$ (CN)$_3$NO] + SO$_4^{2-}$ + 3H$^+$

The overall reaction can be expressed as below

2Co [Fe $^{III}$ (CN)$_3$NO] + 2K$^+$ + HSO$_3^-$ + H$_2$O $\rightarrow$ 2KCo [Fe $^{II}$ (CN)$_3$NO] + SO$_4^{2-}$ + 3H$^+$

**Fig.5.6** Overlaid cyclic voltammograms of n-CoNP modified CPE in absence (a) and in presence (b) of 3.4 mM sulfite: CV response of bare CPE in absence (c) and in presence (d) of 3.4 mM sulfite.

**5.4 Optimization Study**

The experimental variables like pH and electrolyte nature considerably influence the behavior and electrocatalytic efficiency of the CoNP. During the electrochemical reaction, CoNP complex undergoes redox process, hence the charge on the complex changes. Therefore electrolytic cation plays an important role in maintaining the charge neutrality of the
complex. Therefore the variables such as pH, electrolyte and scan rate are systematically studied and optimized. The initial experimental studies were carried out using 0.5 M KNO₃ as an electrolyte at a scan rate of 0.5 Vs⁻¹ scan rate.

5.4.1 Effect of pH
The effect of pH of the electrolyte on the electrochemical behavior of n-CoNP modified electrode was studied by varying the electrolyte pH values ranging from 1 to 8. In all the cases formal potential of redox couple remains unchanged and there was no significant change in the peak current in the pH range 1–5. There after peak currents decreased with increase in the pH value and disappeared at pH 8. Beyond pH 8 no peaks were observed which might be due to the interaction of metal ions present in the complex to form hydroxides. Hence pH of the electrolyte solution was maintained at 5 throughout the studies.

5.4.2 Effect of supporting electrolyte
The cations present in the electrolyte play an important role on the electrochemical behavior of CoNP and its analogues. Electrolyte cations enter or leave the MNP surface to maintain the electroneutrality of the metal nitroprussides during the electrochemical process. The effect of alkali metal cations have been thoroughly studied on the electrochemical behavior of CoNP [49]. In this study the effect of Li⁺, Na⁺ and K⁺ cations by using there respective salt solutions at 0.5 M concentration have been examined. Well defined peaks with high peak current values were observed in case of potassium nitrate. Hence 0.5 M KNO₃ was used as an electrolyte in all investigations of n-CoNP CPE for sulfite quantification using the proposed electrochemical sensor.

5.4.3 Effect of scan rate
The effect of scan rate was studied by varying the sweep rates from 10–1000 mVs⁻¹ (Fig. 5.7 (A)). The peak currents of the voltammogram are linearly related with the scan rate upto 100 mVs⁻¹ (Fig. 7 (B)) indicative of surface confined redox reaction. However at high scan rates i.e. above 100 mVs⁻¹, the peak currents were proportional to the square root of scan rate (Fig.5.7 (C)) which indicates that the process is diffusion controlled. It can be assumed due to relative slow diffusion of cations into a limited reaction layer. The ratio of Iₓₒ and Iₓₒ remains almost equal to unity at different scan rates indicating that the reaction is surface bound in nature.
Fig. 5.7  (A) Overlaid cyclic voltammograms of n-CoNP CPE in 0.5 M KNO₃ at varied scan rates (B) plot of current vs. scan rate.
Fig. 5.7 (C) plot of current vs. square root of scan rate of n-CoNP CPE in 0.5 M KNO$_3$.

Fig. 5.8 (a) shows the cyclic voltammograms of n-CoNP modified carbon paste electrode in 0.5M KNO$_3$ solution at different scan rates in presence of 1mM sulfite.

Fig. 5.8 (A) Overlaid cyclic voltammograms of n-CoNP CPE at different scan rates in presence of 1 mM sulfite
Linear dependence of the peak currents, Ipa and Ipc on the square root of scan rate was obtained (Fig.5.8 (b)). This indicates that the electrode process is controlled by mass diffusion which is suitable behavior for quantitative application.

![Graph](image_url)

**Fig.5.8** (B) plot of current vs. square root of scan rate.

### 5.5 Interference study

The suitability of the developed electrochemical sensor mainly depends on the effect of interfering species present in the real samples along with the analyte. In order to apply the developed sensor for real sample analysis the effect of common interferents that are present in various food samples were studied by spiking these species in the form of its corresponding salts. The organic acids such as ascorbic acid, lactic acid, citric acid, tartaric acid and oxalic acid, sugars such as glucose, fructose, sucrose and some inorganic ions such as bromide, chloride, nitrite, sodium, potassium, carbonate, sulfate etc. were studied at different concentration level.

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Table 5.1  Interference study

<table>
<thead>
<tr>
<th>Interferent</th>
<th>Tolerance limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺, K⁺, SO₄²⁻, CO₃²⁻, Cl⁻, citric, tartaric acid</td>
<td>1000</td>
</tr>
<tr>
<td>Glucose, fructose, sucrose</td>
<td>1000</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>200</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>100</td>
</tr>
<tr>
<td>Bromide</td>
<td>300</td>
</tr>
<tr>
<td>Nitrate</td>
<td>1000</td>
</tr>
<tr>
<td>Nitrite</td>
<td>15</td>
</tr>
<tr>
<td>Nitrite*</td>
<td>200</td>
</tr>
</tbody>
</table>

* Sample was treated with 3 mL of 2% sulfamic acid before its electrochemical measurement.

Among the interfering species studied, nitrite interfered seriously even at 15 ppm level causing more than ± 2% error which was overcome by treating the sample with 3 mL of 2% sulfamic acid. This converts nitrite into nitrogen. Majority of the species did not interfere even at 100 fold excess. The tolerance limits of common interferents are listed in Table 5.1.

5.6 Calibration plot

Potassium nitrate (5 mL of 0.5 M) was transferred into a 10 mL electrochemical cell. The initial and final potentials were adjusted to 0 to 1.0 V vs. Ag/AgCl respectively and the voltammograms were recorded at a scan rate of 0.5 Vs⁻¹. The experiment was repeated in presence of sulfite at different concentrations and the increase in peak current values were proportional to the sulfite concentration (Fig.5.9 (A)). A calibration graph was constructed by plotting the peak currents vs. the sulfite concentration. A linear response was obtained in the concentration range 1–5.9×10⁻⁵ M as well as 2–8×10⁻³ M (Fig.5.9 (B)). The standard deviation (SD) and regression coefficient (r²) values were found to be 0.011, 0.250 and 0.998, 0.98 for lower and higher end calibration graphs respectively. Linear regression equations Y = 1.409 + 8.586 * X and Y= - 0.071 + 0.331 * X are obtained for the lower and higher end
Fig. 5.9  (A) Overlaid voltammograms of n-CoNP CPE in presence of 0, 2, 4, 6, 8 mM sulfite concentrations in 0.5 M KNO₃ as electrolyte at scan rate 0.5 Vs⁻¹ calibration graph respectively. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.4×10⁻⁵ M and 2.29×10⁻⁵ M respectively for the lower end calibration range.

Fig. 5.9  (B) Calibration plot.
5.7 Application Study

The applicability of the proposed electrochemical sensor has been examined by measuring the sulfite content from a variety of food sample matrices such as dry fruits, sugar, wine and water samples. Various sample solutions were prepared following the standard procedure and analyzed by the proposed electrochemical sensor as well as standard iodometric method [50]. The validity of the proposed method has been checked by the recovery study. Known concentrations of standard sulfite were spiked with the samples and total sulfite content was analyzed (Table 5.2).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Proposed method</th>
<th>Total sulphite</th>
<th>Standard method</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original Sulfite</td>
<td>Added Sulfite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugar&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.0±2.3</td>
<td>10</td>
<td>28.8±1.9</td>
<td>30.1±1.8</td>
</tr>
<tr>
<td>Dry grapes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.5±2.1</td>
<td>–</td>
<td>–</td>
<td>19.2±2.3</td>
</tr>
<tr>
<td>Wine&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12.3±2.1</td>
<td>10</td>
<td>21.8±2.0</td>
<td>22.6±1.5</td>
</tr>
<tr>
<td>Tap water&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ND</td>
<td>7.5</td>
<td>7.4±2.0</td>
<td>7.5±1.9</td>
</tr>
<tr>
<td>Drinking water&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ND</td>
<td>3.7</td>
<td>3.8±1.9</td>
<td>4.0±1.8</td>
</tr>
</tbody>
</table>

ND – Not detected

All the values are average of three measurements ±RSD

<sup>a</sup>Concentration of sulfite is expressed in mg/100g

<sup>b</sup>Concentration of sulfite is expressed in mg/100mL
5.8 Conclusions
A simple methodology has been proposed to prepare CoNP nano particles without the use of any additives. The nano CoNP complex was characterized by SEM, FTIR, XRD and CV study. The synthesized CoNP nanoparticles were used as an indicator species towards the electrocatalytic oxidation of sulfite in the form of modified carbon paste electrode. The n-CoNP CPE showed a considerably enhanced electrocatalytic activity in presence of sulfite when compared to s-CoNP and b-CoNP. The n-CoNP modified CPE exhibits one electron transfer process with heterogeneous EC catalytic mechanism. A linear response was obtained in the concentration range 1–5.9×10⁻⁵ M as well as 2–8×10⁻³ M. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.4×10⁻⁵ M and 2.29×10⁻⁵ M, respectively for the lower end calibration range. The proposed CPE showed a good linear range and low detection limit, when compared with some of the reported electrochemical methods.

5.9 References
22. FDA Federal Register, 51, 131, 25021, (9 July 1986).