A NEW HYDRAZONE DERIVATIVE AS A SENSITIVE ANALYTICAL REAGENT FOR THE DETERMINATION OF Co(II) IN FOOD, WATER AND SYNTHETIC SAMPLES

P. Nityananda Kumar Reddy ¹, G. Trivikram Reddy ², Sangita D. Kumar ³, A. V. R. Reddy ³, S. Nazneen Parveen ¹, and N. C. Gangi Reddy ²

Department of Environmental Sciences ¹, Department of Chemistry ², Yogi Vemana University, Kadapa – 516 003, A.P., India.
Analytical Chemistry Division ³, Bhabha Atomic Research Centre (BARC) Trombay- 400 085, Mumbai, Maharashtra, India.

ABSTRACT: A novel (N', N"E, N', N"E) - N', N" - (2, 2' - (propane-1,3-diylibis(sulfanediyl))bis(1-(4-chlorophenyl) ethan – 2 – yl – 1 -yldiene))bis(2-hydroxybenzohydrazide)(CAPSH) is identified as a sensitive and selective analytical reagent for the determination of trace levels of Co(II) in environmental samples like in food, water, synthetic samples and medicinal plants by spectrophotometry. CAPSH reacts with cobalt(II) at pH 7.0, in aqueous DMF to form orange colored 1:1 (Co-CAPS) complex shows maximum absorbance (λₘₐₓ) at 380nm. The color reaction is immediate and the absorbance remains constant for about 24h. The molar absorptivity coefficient and Sandell’s sensitivity are found to be 7.9×10⁴ L.mol⁻¹ cm⁻¹ and 0.048μg cm⁻² of cobalt(II) respectively. The linear regression coefficient is 0.9998 and standard deviation is 0.0050. The system obeys Beer’s law in the range of 0.059-0.59μg mL⁻¹ of cobalt(II). Large number of cations, anions and complexing agents do not interfere in this method. This method is successfully applied for the determination of cobalt(II) in environmental samples like food, water (potable and polluted), synthetic samples and medicinal plants.

INTRODUCTION: Cobalt is one of the most important micro nutrients in animals and humans ¹, ². It is a part of vitamin B12 (cobalamin), which is the primary biological reservoir of cobalt as an "ultra trace" element. The recommended dietary allowance (RDA) of vitamin B12 for adults is 2.4 μg per day, which contains 0.1 μg of cobalt and its deficiency can lead to pernicious anemia ³.

Vitamin B12 is also helpful in the metabolism of every cell of the human body, particularly affecting DNA synthesis, fatigue, digestive disorders, neuromuscular problems and is essential for the formation of red blood cells. Deficiency of cobalt leads to various diseases such as pernicious anemia, cardiovascular, neuropsychiatric and hematologic disorders ⁴.

Absorption of excess of inorganic cobalt for a long period of time lead to serious health problems such as over production of red blood cells, thickened blood, thyroid, cardiomyopathy and increased activity in the bone marrow ⁵. In addition, cobalt also used in the production of catalysts, batteries, permanent magnets, pigments for enamels and...
Among these, the spectrophotometric methods are preferred as they are cheaper, suitable for automation and have comparable sensitivity. A number of hydrazone derivatives are used as spectrophotometric reagents for the determination of various metal ions for the past few decades. The extensive literature studies reveal that only a few hydrazones of carbonyl compounds have been used for the spectrophotometric determination of Co(II)\(^{6-18}\). However, the reported spectrophotometric methods\(^{6-18}\) suffer from one or more disadvantages such as severe interferences, less sensitivity and less selectivity etc. Nevertheless, none has been reported on spectrophotometric determination of Co(II) in food, water, synthetic samples and medicinal plants using \((N',N''E,N',N''E)-N,N''E-(2,2'- (propane-1,3-diylbis(sulfanediyl)) bis (1-(4-chlorophenyl)ethan-2-yl-1-ylidene))bis(2-hydroxy benzohydrazide)\) (CAPSH) as a sensitive analytical reagent.

Herein, we identified a new hydrazone derivative (CAPSH) as a sensitive and selective analytical reagent for the spectrophotometric determination of Co (II) in food, water and synthetic samples. The present method is highly sensitive and selective when compared to the previously reported methods (Table 1).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reagent</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>pH</th>
<th>Beer’s law (ppm)</th>
<th>(\varepsilon \times 10^4) L.mol(^{-1})cm(^{-1})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2-Benzimidazolyl-3-sulphophenyl methanone-5-nitro-2-pyridyl-hydrazone</td>
<td>517</td>
<td>2.7-9.4</td>
<td>0.02-1.00</td>
<td>6.65</td>
<td>6</td>
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<tr>
<td>2.</td>
<td>3,4- Dihydroxybenzaldehyde guanylhydrazone</td>
<td>335</td>
<td>-</td>
<td>0.5-16.00</td>
<td>0.29</td>
<td>7</td>
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<td>3.</td>
<td>2-Hydroxybenzaldehyde-5-nitropyridylhydrazone</td>
<td>470</td>
<td>-</td>
<td>0.02-1.5</td>
<td>6.5</td>
<td>8</td>
</tr>
<tr>
<td>4.</td>
<td>p-Methylinositrosoacetophenone hydrazone</td>
<td>520</td>
<td>7.5</td>
<td>0.2-6.0</td>
<td>1.83</td>
<td>9</td>
</tr>
<tr>
<td>5.</td>
<td>2-Pyridine carboxaldehyde isonicotinyl-hydrazine</td>
<td>346</td>
<td>9.0</td>
<td>0.01-2.7</td>
<td>7.1</td>
<td>10</td>
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<tr>
<td>6.</td>
<td>2-Hydroxy-1-naphthaldene salicyloyl hydrazone</td>
<td>430</td>
<td>8.0-9.0</td>
<td>0-10</td>
<td>0.16</td>
<td>11</td>
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<td>7.</td>
<td>Pyridine-2-acetaldehyde salicyloyl hydrazone</td>
<td>415</td>
<td>1.0-6.0</td>
<td>0.5-7.0</td>
<td>1.04</td>
<td>12</td>
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<td>8.</td>
<td>2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone</td>
<td>425</td>
<td>5.0</td>
<td>0.12-3.54</td>
<td>2.3</td>
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<td>9.</td>
<td>Pyridine-2-aldehyde2-quinolylhydrazone</td>
<td>510</td>
<td>6.5-11.5</td>
<td>-</td>
<td>3.00</td>
<td>14</td>
</tr>
<tr>
<td>10.</td>
<td>2-Benzoylpyridine2-pyridylhydrazone</td>
<td>478</td>
<td>3.85-11.6</td>
<td>-</td>
<td>2.93</td>
<td>15</td>
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<td>11.</td>
<td>Benzil mono(2-pyridyl)hydrazone</td>
<td>535</td>
<td>8.0</td>
<td>-</td>
<td>2.74</td>
<td>16</td>
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<td>12.</td>
<td>2,2’Dipyridyl 2- pyridyl hydrazone</td>
<td>480-500</td>
<td>3.0 -11.0</td>
<td>-</td>
<td>3.2-4.2</td>
<td>17</td>
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<tr>
<td>13.</td>
<td>Eosin Biacetyl .mono(2-pyridyl)-hydrazone</td>
<td>505</td>
<td>6.0</td>
<td>-</td>
<td>2.35</td>
<td>18</td>
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<tr>
<td>14.</td>
<td>((N',N''E,N',N''E)-N,N''E-(2,2'- (propane-1,3-diylbis(sulfanediyl))bis(1-(4-chlorophenyl)ethan-2-yl-1- ylidene))bis(2-hydroxy benzohydrazide))</td>
<td>380</td>
<td>7.0</td>
<td>0.059-0.59</td>
<td>7.9</td>
<td>PM</td>
</tr>
</tbody>
</table>
MATERIALS AND METHODS:
Apparatus and Reagents:
A Double beam UV-Visible spectrophotometer (Shimadzu model UV-2203) with a 1.0 cm quartz cell is used for absorbance studies and pH meter (Systronics model 3305) is used for measurement of pH respectively. Melting point is determined and is uncorrected. Results are compared with the data generated for the same using inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer Élan DRCII ICP-MS Toronto, Ontario, Canada), flame atomic absorption spectrophotometer (Shimadzu model No. AA-6300).

$^1$H NMR spectrum is recorded on Jeol 400 MHz NMR Spectrometer JNM-400) and Mass spectrum is recorded on Shimadzu-LCMS with ESI probe (LC-2010EV). All the chemicals used are of analytical reagent grade or the highest purity available (Across or Merck). DMF and Double distilled water are used throughout analysis.

Preparation of (N', N''E, N', N''E)-N', N'-(2, 2'-(propane - 1, 3- diylbis (sulfanediyl))) bis (1 - (4-chlorophenyl) ethan-2-yl-1ylidene)) bis (2hydroxy benzohydrazide) (CAPSH) (III): 2,2'-(propane-1,3-diylbis (sulfanediyl)) bis (1-(4-chlorophenyl) ethanone) (I) [2.0 gm, 4.8 mmol] and salicylic acid hydrazide (II) [1.461gm, 9.6 mmol] and 20 mL ethanol are taken into a 100-mL two necked RB flask. The reaction mixture is stirred at reflux temperature for 8 hrs. The progress of the reaction is monitored by TLC. After completion of the reaction, the solvent is removed under reduced pressure. The formed product (III) is washed with a mixture of water and ethanol, filtered and dried. The obtained crude product is recrystallised from hot solution of aq. ethanol and dried. The structure of newly synthesized hydrazone is confirmed by $^1$H NMR and Mass spectral data.

Characterization data of CAPSH:
Colour: Light yellow; yield: 2.5 gm (75.8%); mp: 223°C; 1H NMR (400 MHz, DMSO-d6): δ11.65 (s, 2H, arom-OH), 11.55 (s, 2H, NH), 7.97 (d, 2H, J= 6 Hz, H), 7.87 (d, 4H, J=8.4 Hz, H), 7.49 (d, 4H, J=8.5 Hz, H), 7.20 (t, 2H, J=7.6 Hz, H), 7.03 (d, 2H, J=8.0 Hz, H), 6.98 (t, 2H, J=7.6 Hz, H), 3.89 (s, 4H, 2-N=C=CH2-S), 2.59 (t, 4H, J=7.2 Hz, 2-S-CH2-), 1.80 (quint, 2H, J = 6.8 Hz, -CH2-CH2-CH2); MS (ESI): (M+H)$^+$ 682.

$^1$H-NMR spectrum of (N', N''E, N', N''E)-N', N'-(2, 2'-(propane-1, 3-diylbis (sulfanediyl))) bis (1-(4-chlorophenyl) ethan-2-yl-1ylidene)) bis (2hydroxy benzohydrazide).
Preparation of 0.01M CAPSH solution:
681.7mg of reagent is dissolved in 100-mL standard flask with DMF and made up to the mark. Further, required dilutions are prepared from this solution.

Preparation of cobalt (II) stock solution:
0.01M cobalt solution is prepared by dissolving 238mg of cobalt chloride(Merck) in de-ionised water containing few drops of concentrated hydrochloric acid and made up to the mark in a100-mL volumetric flask. Aliquots of this solution are standardized with EDTA using xylenol orange as an indicator. Dilute solutions are prepared from this stock solution. Solutions of large number of inorganic ions and complexing agents are prepared from their analytical grade or equivalent grade, water soluble salts.

Preparation of Buffer solutions:
Hydrochloric acid (1M) and sodium acetate (1M) are mixed to get the required pH (1.0-3.5); 0.2M sodium acetate and 0.2M acetic acid are mixed to get the required pH (4.0-6.0), ammonium acetate buffer (pH 7.0) solution is used, 0.1M sodium benzoate solution (pH8) is used and 0.05M borax solution (pH 9.18) is used. The pH of the above buffer solutions are measured by a pH meter and finally adjusted suitably.

General analytical procedure for the determination of cobalt (II):
An aliquot (1.0 mL) of the solution containing known amount of cobalt (II), 4.0 mL of ammonium acetate buffer solution (pH7.0), 1.0 mL of DMF and 1.0 mL of CAPSH reagent of required concentration are mixed in a 10-mL volumetric flask and the resulting solution is diluted up to the mark with double distilled water. The absorbance of this solution is measured at 380nm, against the reagent blank.

RESULTS AND DISCUSSION:
CAPSH reacts with cobalt (II) and forms an orange colored complex in aqueous DMF at pH 7.0. The Co-CAPSH complex shows maximum absorbance (λmax) at 380nm against the reagent blank. Hence, a detailed study has been undertaken for the determination of cobalt (II) using CAPSH by spectrophotometric method. The optimized method is successfully applied for the determination of cobalt in food, water, synthetic samples and medicinal plants alone or in presence of diverse ions.

Absorption spectra of ligand (CAPSH) and Co (II)-CAPSH complex (MLC):
Absorption spectrum of the CAPSH is recorded against the solvent blank initially. The absorption spectrum of Co(II)-CAPSH complex is recorded against the reagent blank. The absorption spectrum
of both complex and reagent are shown in Fig.1. From the absorption spectra, it is clear that the reagent shows maximum absorption at 315 nm, whereas the complex shows maximum absorption at 380nm. Therefore, all the spectral measurements are carried out at 380 nm.

![Absorption Spectra](image)

**FIG. 1:** (A) ABSORPTION SPECTRUM OF REAGENT (CAPSH) VS. SOLVENT (DMF) BLANK
(B) Absorption spectrum of Co (II)-CAPSH complex (MLC) Vs. reagent blank; Co (II) =1.0mL of 1.0x10^-4M, CAPSH = 1.0 mL of 1.0x10^-4M and pH = 7.0.

**Effect of pH:**

In to a series of 10-mL volumetric flasks, 1.0 mL of Co(II) solution (1.0x10^-4M), 1.0 mL of reagent solution (1.0x10^-4M), 1.0mL of DMF and 4.0 mL of buffer of varying pH (1.0-9.0) are added and made up to the mark with double distilled water and the absorbance is measured against reagent blank at 380nm. From this study, it is found that the pH 7.0 is the optimum pH (Fig.2) and this pH is used for all the experiments.

![Effect of pH](image)

**FIG.2: EFFECT OF PH ON THE ABSORBANCE OF CO(II)-CAPSH COMPLEX; Co(II) = 1.0 mL of 1.0x10^-4 M; CAPSH =1.0 mL of 1.0x10^-5 M; λ_max = 380nm**

**Applicability of Beer’s law:**

The known aliquots of 10 mL solutions, each containing constant volumes of 4.0 mL of buffer (pH 7.0), 1.0 mL of 1.0x10^-4M of reagent and 1.0 mL of cobalt(II) solutions of concentrations in the range from 0.10x10^-4 M to 1.0x10^-4M (0.059-0.59μg mL^-1) are prepared. The absorbance of these solutions is measured at 380nm. A graph plotted
between the amount of cobalt (II) and its absorbance is shown in Fig. 3. From the graph, it is found that, a linear plot passing through the origin obeys Beer’s law in the range from 0.059-0.59 μg mL⁻¹ of cobalt (II). The correlation coefficient is 0.99959 which indicates the linearity between the two variables. The molar absorptivity coefficient and Sandell’s sensitivity of the complex are found to be 7.9×10⁴ L mol⁻¹ cm⁻¹ and 0.048μg cm⁻² respectively.

**Job’s method of continuous variation:**

Equi-molar solutions of cobalt (II) ion and reagent CAPSH (1.0×10⁻⁴M concentration each) is prepared. The metal and reagent solutions are mixed in different proportions, keeping the total volume of metal and reagent is constant at 5.0 mL. In each case, 4.0 mL of ammonium- acetate buffer (pH 7.0) is added to the mixture and the total volume of the solution is made up to 10.0 mL with double distilled water.

The absorbance of all the solutions is measured at 380 nm against their reagent blanks. The corresponding graph (Fig. 4) is drawn between absorbance and \( V_n/V_{l} + V_m \) (where \( V_1 \) and \( V_m \) are the volumes of the reagent and the metal, respectively) indicates that one mole of cobalt(II) reacts with one mole of reagent and the composition of metal to reagent as 1:1 ratio (Fig. 4). The composition of the M-L complex is further confirmed by Molar ratio method (Fig. 5&6).

**Mole ratio method:**

*Effect of ligand concentration:*

In to a 10-mL volumetric flask 1.0 mL of 1.0×10⁻⁴ M Co(II) solution, 4.0 mL of pH 7.0 buffer,1.0 mL of varying amounts of (1×10⁻⁵ to 2.0×10⁻⁴ M) reagent (CAPSH) and 1.0mL of DMF are added then made up to the mark with water and measured the absorbance at 380nm against the corresponding reagent blanks. A graph is drawn between absorbance and molar proportion of the reagent to that of metal ion (Fig. 5). From the graph, it is observed that 1.0 mole of reagent is necessary for the maximum recovery of 1.0 mole of Co (II), which is in good agreement with the results of Job’s method of continuous variation.
Effect of metal ion concentration:
Different molar excess of Co(II) are added to the fixed amount of CAPSH and absorbance is measured according to the standard procedure. It is observed that the reagent and metal molar ratio is 1:1. Based on the above two methods the composition of the Co(II)-CAPSH complex is confirmed as 1:1 ratio (Fig. 6).

![Effect of Metal conc.](image)

**FIG. 6: EFFECT OF METAL CONCENTRATION: CAPSH = 1.0 mL of (1.0 x 10^{-4} M), Co (II) = 1.0 mL of (0.1 x 10^{-5} - 2.0 x 10^{-4} M), pH = 7.0 and \( \lambda_{\text{max}} = 380 \text{nm} \)**

Effect of foreign Ions:
The effect of various cations and anions which are generally associated with the metal ion on the determination of the cobalt (II) is studied by measuring the absorbance of the cobalt complex containing 1 µg mL⁻¹ of cobalt (II) in solution. The effect of foreign ions on complexation is studied by taking 1.0 mL of Co (II) solution, 1.0 mL of required concentration of the foreign ion solution, 4.0 mL of ammonium acetate buffer (pH 7.0), 1.0 mL of CAPSH solution and 1.0 mL of DMF in a 10.0 mL standard flask. The total volume of the solution is brought to 10 mL with double distilled water. The experiment is repeated by changing the concentration of the diverse ion. The absorbance is measured at 380 nm. A change of ± 0.02 is taken as the tolerance limit for interference. The results indicated that Ca(II), Mg(II), Pb(II) and Mn(II) do not interfere even when present up to 10000 µg. Interference due to Al(III) and Cr(III) can be tolerated up to 5000 µg, whereas Mo(vi) and W(v) can be tolerated up to 2500 µg only. Extraction of cobalt(II) is not possible in the presence of Cu(II), Ni(II), Fe(II)/Fe(III), Zn(II), Pd(II), and Cd(II), due to their severe interference, even when present in trace amount. Anions such as fluoride, bromide, chloride, nitrate, sulfate, thio-sulfate and acetate do not affect the extraction of cobalt (II), even when present up to 5000 µg. In the presence of thiocyanate and oxalate, extraction of cobalt(II) is not possible. 1.0 mL of 0.2% sodium fluoride has been used as a masking agent for Fe(III) and 1.0% potassium iodide for Ni(II), Cu(II). Zn(II) and Cd(II) do not interfere in the pH range studied.

Scope of the method:
The present method is successfully applied to the determination of cobalt when present alone or in presence of diverse ions. The method is also extended to the determination of cobalt in food, water, synthetic samples and medicinal plants.

Determination of cobalt in water samples:
Different water samples are collected from in and around Kadapa. A.P., India and Bay of Bengal, Nellore. Each filtered water samples is evaporated nearly to dryness with a mixture of 5.0 mL of concentrated H₂SO₄ and 10.0 mL of concentrated HNO₃ in a fume cupboard and then cooled to room temperature. The residue is then heated with 10.0 mL of double distilled water, in order to dissolve the salts. The solution is cooled and neutralized with dilute NH₄OH in the presence of 1.0 – 2.0 mL of 0.01% (w/v) tartrate solution. The resulting solution is filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with double distilled water. The results obtained are comparable with those values determined (Table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cobalt Spiked (µg/L)</th>
<th>Conc. of Co(II) by AAS method (µg/L)</th>
<th>Conc. of Co(II) by present method (µg/L)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water ¹</td>
<td>100</td>
<td>100.036</td>
<td>100.034</td>
<td>100.034%</td>
</tr>
<tr>
<td>Waste water ²</td>
<td>100</td>
<td>100.028</td>
<td>100.027</td>
<td>100.027%</td>
</tr>
<tr>
<td>Tap water ³</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000%</td>
</tr>
</tbody>
</table>

¹Bay of Bengal, Nellore.; ²Collected from industrial area, Kadapa.; ³Yogi Vemana University, Kadapa

TABLE 2: DETERMINATION OF CO(II) IN WATER SAMPLES
Determination of cobalt in food samples and medicinal plants:
Food samples and medicinal plants are collected from various villages around Kadapa, A.P. India. The samples are cleaned and dried in open air, and are covered with a neat to protect them from mineral contamination. The dried samples are pulverized in a mortar to convert into convenient size. One gram of powdered food sample is taken in a 100-mL beaker and digested with 10.0 mL of concentrated nitric acid and hydrochloric acid. Further add 10.0 mL of double distilled water and then filtered by using whatmann No.41 filter paper. The filtrate is taken in a 10-mL standard flask made up to the mark with double distilled water and analyzed as per the optimized procedure. The results obtained are comparable with those values determined (Table 3 and Table 4).

### TABLE 3: CONCENTRATION LEVELS OF CO(II) IN FOOD SAMPLES

<table>
<thead>
<tr>
<th>S No.</th>
<th>Name of the food sample</th>
<th>Cobalt spiked (µg/L)</th>
<th>Conc. of Co(II) by ICP-MS method (ppm)</th>
<th>Conc. of Co(II) by present method* (ppm)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wheat grain (Triticum aestivum)</td>
<td>100</td>
<td>100.01</td>
<td>100.01</td>
<td>100.01</td>
</tr>
<tr>
<td>2</td>
<td>Cabbage (Brassica oleracea)</td>
<td>100</td>
<td>100.03</td>
<td>100.02</td>
<td>100.02</td>
</tr>
<tr>
<td>3</td>
<td>Carrot (Daucas carota)</td>
<td>100</td>
<td>100.02</td>
<td>100.01</td>
<td>100.01</td>
</tr>
<tr>
<td>4</td>
<td>Potato (Solanum tuberosum)</td>
<td>100</td>
<td>100.02</td>
<td>100.02</td>
<td>100.02</td>
</tr>
<tr>
<td>5</td>
<td>Tomato (Lycopersicon esculentum)</td>
<td>100</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>6</td>
<td>Beet root (Beta vulgaris)</td>
<td>100</td>
<td>100.05</td>
<td>100.04</td>
<td>100.04</td>
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<tr>
<td>7</td>
<td>Raddish (Raphanus sativus)</td>
<td>100</td>
<td>100.04</td>
<td>100.04</td>
<td>100.04</td>
</tr>
<tr>
<td>8</td>
<td>Cauliflower (Brassica oleracea)</td>
<td>100</td>
<td>100.06</td>
<td>100.06</td>
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<td>9</td>
<td>Groundnut (Arachis hypogaea)</td>
<td>100</td>
<td>100.08</td>
<td>100.07</td>
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<td>10</td>
<td>Rumex vesicarius (Chukaku)</td>
<td>100</td>
<td>100.17</td>
<td>100.17</td>
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</tr>
<tr>
<td>11</td>
<td>Spinacia oleracia (Palakura)</td>
<td>100</td>
<td>100.03</td>
<td>100.02</td>
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<tr>
<td>12</td>
<td>Amaranthus graecizans (Cirraku)</td>
<td>100</td>
<td>100.08</td>
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<td>13</td>
<td>Amaranthus cruentus (Thotakura)</td>
<td>100</td>
<td>100.06</td>
<td>100.05</td>
<td>100.05</td>
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<tr>
<td>14</td>
<td>Coriandrum sativum (Kothimera)</td>
<td>100</td>
<td>100.09</td>
<td>100.08</td>
<td>100.08</td>
</tr>
<tr>
<td>15</td>
<td>Hibiscus cannabinus (Gongura)</td>
<td>100</td>
<td>100.05</td>
<td>100.04</td>
<td>100.04</td>
</tr>
</tbody>
</table>

*Average of five readings

### TABLE 4: DETERMINATION OF CO(II) IN MEDICINAL PLANTS

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Name of the plant</th>
<th>Conc. of Co(II) by ICP-MS method (µg/mL)</th>
<th>Conc. of Co(II) by present method* (µg/mL)</th>
<th>STD (µg/mL)</th>
<th>% of RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phillanthus amarus</td>
<td>2.470 [22]</td>
<td>2.468</td>
<td>0.0014</td>
<td>0.0573</td>
</tr>
<tr>
<td>2</td>
<td>Tinospora cardifolia</td>
<td>0.546 [23]</td>
<td>0.544</td>
<td>0.0014</td>
<td>0.2595</td>
</tr>
<tr>
<td>3</td>
<td>Eclipta alba</td>
<td>1.921 [23]</td>
<td>1.918</td>
<td>0.0021</td>
<td>0.1105</td>
</tr>
<tr>
<td>4</td>
<td>Asparagus racemosus</td>
<td>0.861 [24]</td>
<td>0.858</td>
<td>0.0021</td>
<td>0.2468</td>
</tr>
<tr>
<td>5</td>
<td>Emblica officinalis</td>
<td>0.364 [24]</td>
<td>0.362</td>
<td>0.0014</td>
<td>0.3895</td>
</tr>
</tbody>
</table>

*Average of five reading

Preparation of synthetic samples:
Metal ion solutions of Cu²⁺, Fe²⁺, Pb²⁺, Ni²⁺, Mn²⁺, Zn²⁺, Hg²⁺, Pd²⁺, Cd²⁺ and Co²⁺ are prepared from Merck analytical grade stock standards of concentration 1000µg/mL. The synthetic water solutions are then prepared by mixing the different metal ions as prescribed in the Table 5. The aliquot is analyzed for Co(II), by adopting the recommended procedure. The results obtained are comparable with those values determined (Table 5).

### TABLE 5: DETERMINATION OF CO(II) IN SYNTHETIC SAMPLES

<table>
<thead>
<tr>
<th>Samples</th>
<th>Metal 1 (µg/mL)</th>
<th>Metal 2 (µg/mL)</th>
<th>Metal 3 (µg/mL)</th>
<th>Metal 4 (µg/mL)</th>
<th>AAS method (µg/mL)</th>
<th>Present method* (µg/mL)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe</td>
<td>Hg</td>
<td>Ni</td>
<td>Co</td>
<td>3.99</td>
<td>3.98</td>
<td>99.50</td>
</tr>
<tr>
<td>2</td>
<td>Hg</td>
<td>Ni</td>
<td>Mn</td>
<td>Co</td>
<td>3.98</td>
<td>3.98</td>
<td>100.00</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>Zn</td>
<td>Ni</td>
<td>Co</td>
<td>3.97</td>
<td>3.96</td>
<td>99.00</td>
</tr>
<tr>
<td>4</td>
<td>Cd</td>
<td>Pb</td>
<td>Ni</td>
<td>Co</td>
<td>3.96</td>
<td>3.95</td>
<td>98.75</td>
</tr>
<tr>
<td>5</td>
<td>Cu</td>
<td>Pd</td>
<td>Mn</td>
<td>Co</td>
<td>3.98</td>
<td>3.98</td>
<td>100.00</td>
</tr>
</tbody>
</table>

*Average of five readings
CONCLUSION: A novel hydrazone derivative identified as a highly sensitive and selective analytical reagent for the determination of Co(II) in food, water, synthetic samples and medicinal plants by simple spectrophotometric method. It can be used as an alternative method for routine quality control analysis of Co (II). The molar absorptivity of the complex (7.9×10^4 L mol⁻¹cm⁻¹) reveals that the ligand is highly sensitive for the determination of Co(II) when compared with other hydrazones. A number of associated elements don’t interfere in the determination of cobalt. Hence, CAPSH is an alternative ligand for the spectrophotometric determination of low and trace levels Co(II). The proposed method offers advantages like good sensitivity, selectivity, reliability, reproducibility, less interference and immediate color development. The developed method is found to be quantitative comparable to other standard methods.

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