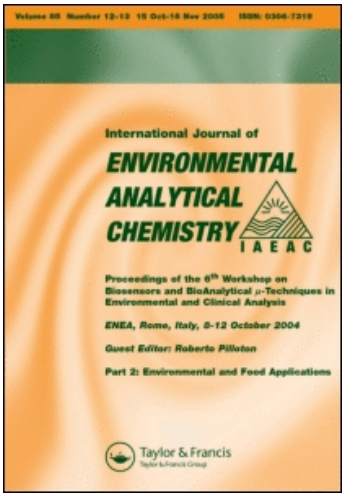


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# A novel spectrophotometric method for determination of cyanide using cobalt (II) phthalocyanine tetracarboxylate as a chromogen

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Cobalt (II) phthalocyanine tetracarboxylate [Co (II)Pc-COOH] has been prepared and used in aqueous solutions as a novel chromogenic reagent for the spectrophotometric determination of cyanide ion. The method is based on measuring the increase in the intensity of the monomer peak in the reagent absorbance at 682 nm due to the formation of a 1 : 2 [Co (II)Pc-COOH] : [CN] complex. The complex exhibits a molar absorptivity ($\varepsilon$) of $7.7 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ and a formation constant ($K_f$) of $5.4 \pm 0.01 \times 10^6$ at $25 \pm 0.1$°C. Beer's law is obeyed over the concentration range 0.15–15 μg mL$^{-1}$ ($5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M) of cyanide ion, the detection limit is 20 ng mL$^{-1}$ ($7.7 \times 10^{-7}$ M) the relative standard deviation is ±0.7% ($n = 6$) and the method accuracy is $98.6 \pm 0.9$%. Interference by most common ions is negligible, except that by sulphite. The proposed method is used for determining cyanide concentration in gold, silver and chromium electroplating wastewater bath solutions after a prior distillation with 1 : 1 $H_2SO_4$ and collection of the volatile cyanide in 1 M NaOH solution containing lead carbonate as recommended by ASTM, USEPA, ISO and APAHE separation procedures. The results agree fairly well with potentiometric data obtained using the solid state cyanide ion selective electrode.

**Keywords:** electroplating wastewater; cobalt (II) phthalocyanine tetracarboxylate chromogen; spectrophotometry; determination of cyanide



## 1. Introduction

Cyanides are toxic pollutants to aquatic life, which interfere with normal biological processes of natural purification in streams, present a hazard to agricultural uses of water and are a menace to public water supplies and bathing. While cyanide compounds are widely used in industry, metal plating is responsible for most of the cyanide wastes causing stream pollution [1–4]. Various instrumental techniques have been suggested for determining cyanides, including the use of potentiometric sensors [5–10], chromatography [11,12], spectrofluorimetry [13], indirect atomic absorption spectrometry [14] and spectrophotometry [15–26].

The most commonly used methods for cyanide quantification are based on spectrophotometry. Conversion of cyanide into cyanogen chloride (König reaction) followed by the interaction with pyridine to form glutaconic aldehyde which gives a blue-coloured dye with 1-phenyl-1, 3-methy-1 and 5-pyrazolone has been described [15]. However, this

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method involves several time-consuming reaction steps. Many other chromogens such as arylidenerhodamines [16], metallo-porphyrins [17,18], 2,2-dihydroxy-1,3-indanedione [19–21], 2,2′-dipyridyl-2-quinolylhydrazone (DPQH) [22], phenolphthalein [23], isonicotinate-3-methyl-1-phenyl-2-pyrazolin-5-one [24], pyridine-barbituric acid [25], and diaquocobester [26] have been suggested. Most of these methods, however, involve several derivatisation reactions [15], long reaction time [22], or suffer from reagent instability [15,19,20], applicability over a narrow concentration range [16,19,20,26] and interferences by $SO_4^{2-}$, $SO_3^{2-}$, $S^{2-}$, $NO_3^-$, $NO_2^-$, $SCN^-$ and $CO_3^{2-}$ [17,19,20,27].

Although metallo-phthalocyanines (MPc) are stable, inexpensive reagents with high affinity towards many anions including cyanide ion [28–30], little is known about their use as chromogens for spectrophotometric determination of cyanides due to their poor solubility in aqueous solutions. In the present work, the hydrophilicity of such compounds was increased by introducing of four hydrophilic carboxylic groups on the terminal positions of cobalt phthalocyanine ring to obtain a water-soluble tetracarboxylate derivative. The reagent can thus be used for simple, fast, sensitive and selective spectrophotometric determination of low levels of cyanide concentration. The method has successfully been applied to determine cyanides in wastewater samples of various electroplating baths. Results with a mean relative standard deviation of ±1.3% and comparing favourably with potentiometric data are obtained.



## 2. Experimental

### 2.1 *Apparatus*

A spectrophotometer (Shimadzu, Model 1601) was used for the spectrophotometric measurements. The pH measurements were made using a combination glass pH electrode (Orion, Model 81-02) and a double channel pH/mV meter (Orion, Model SA 720). A solid-state cyanide ion-selective electrode (Orion, Model 94-06A) in conjunction with a double junction Ag/AgCl reference electrode (Orion, Model 90-02) was used for the direct measurements of cyanide ion. A glass distillation system for cyanide (Wheaton, UK) was used.

### 2.2 *Reagents and chemicals*

Cobalt (II) phthalocyanine tetracarboxylate (tetrabenzoporphyrazin-4,4′,4″,4‴-tetracarboxylic acid, molecular mass 747), was synthesised by mixing of 12.0 mM of cobalt sulphate, 60.0 mM of 1, 4-phthalic acid and 500.0 mM of urea. Ammonium molybdate catalyst (0.10 mM) was added and the mixture was refluxed in 100.0 mL of nitrobenzene at 170°C for 4 hours. The solid product was filtered off while hot and digested in a boiling water/ethanol solution (50% v/v). The precipitate was washed several times with hot ethanol followed by hot water and dried in a well ventilated dry oven at 80°C. The crude material was dissolved in 25 mL of 1 M NaOH followed by 25 mL of 1 M $H_2SO_4$ to remove the soluble by-products and unreacted materials. The purified product was then dissolved in concentrated sulphuric acid while stirring, then poured slowly over crushed ice. The obtained pure pigment was precipitated and allowed to stand in solution overnight. The precipitate was then filtered off through a sintered-glass funnel (G4), washed with distilled water until sulphate-free filtrate was obtained. The precipitate was washed with ethanol, ether, and dried at 105°C. Elemental analyses confirmed the formation of $C_{36}H_{16}N_8O_8Co$

(calculated C, 62.52%; H, 2.32%; N, 8.52%, found C, 62.3%, H, 2.2%; N, 8.0%). The complex displayed an absorption peak at 660 nm due to the Q-band of metal-phthalocyanine monomeric species [31]. The infrared spectrum exhibited stretching vibrations at 1697 and 3337 $cm^{-1}$ assigned to the $\upsilon$C=O and $\upsilon$ –OH groups of the carboxylic acids.

Sodium cyanide and sodium hydroxide were obtained from Aldrich Chemical Company (Milwaukee, WI). A stock 1000 $\mu g\,mL^{-1}$ of aqueous cyanide solution was freshly prepared in 0.05 M NaOH. The solution was standardised by potentiometric titration with a standard silver nitrate as described previously [32]. A 100 mL solution of Co (II) phthalocyanine tetracarboxylate reagent (20 $\mu g\,mL^{-1}$ in NaOH) was freshly prepared by dissolving 2.0 mg of the reagent in 10 mL of 0.05 M NaOH solution. The solution was diluted to 100 mL in a volumetric flask. All reagents were prepared from analytical reagent grade chemicals unless otherwise specified and doubly distilled deionised water was used throughout.

### 2.3 *Calibration of cyanide*

Calibration curve of cyanide was prepared by transferring 1.0 mL aliquot of the reagent to a 1.0 cm path length cuvette (4 mL total volume) followed by addition of 1.0 mL of 0.3–30 $\mu g\,mL^{-1}$ ($1.2 \times 10^{-5}$–$1.2 \times 10^{-3}$ M) aqueous cyanide calibrants in separate runs. After shaking the solutions for 3 min at $25 \pm 0.1^{\circ}C$ to effect complete mixing, the absorption spectra were recorded for the different cyanide concentrations in the range 500–900 nm. A blank experiment was run under similar conditions using 1.0 mL of 0.05 M NaOH instead of the cyanide solution. The intensities at the maximum absorption of 682 nm of the reagent and the reagent plus cyanide were recorded and the differences were plotted against cyanide concentration.



### 2.4 *Formation constant of the cyanide complex*

Formation constant of {[Co (II) phthalocyanine tetracarboxylate] [cyanide]} complex was measured at $25 \pm 0.1^{\circ}C$ by using the standard spectrophotometric method [29,33] and calculated according to Equation (1):

$$\mathrm{Log}[(A_x - A_o)/(A_\infty - A_x)] = \log K + n \log[CN^-] \quad (1)$$

where $A_x$ is the equilibrium absorbance at 682 nm, $A_o$ is the absorbance of Co (II) phthalocyanine tetracarboxylate solution at 682 nm before addition of cyanide, and $A_\infty$ was the absorbance with the highest cyanide concentration at the same wavelength. A relation between log $[(A_x - A_o)/(A_\infty - A_x)]$ and log $[CN^-]$ was plotted. The $y$-axis intercept indicates the formation constant ($K_f$) of the complex.

### 2.5 *Tolerance of acid releasing anions*

The effect of volatile acid releasing anions other than cyanide on alkaline Co (II) phthalocyanine tetracarboxylate reagent solution was checked at 682 nm. Aliquots (1.0 mL) of $1.0 \times 10^{-2}$ M aqueous solutions of $N_3^-$, $NO_2^-$, $S^{2-}$, $CO_3^{2-}$, and $SO_3^{2-}$ ions were added to 1.0 mL of 20 $\mu g\,mL^{-1}$ Co (II) phthalocyanine tetracarboxylate solution in the quartz cuvette. The solutions were mixed and the absorbance read at 682 nm for

each anion. The tolerance of these ions was calculated. Tolerance is defined as the maximum weight ratio of foreign ion to $CN^-$ producing an error of ±5% in the determination of $10\,\mu g\,mL^{-1}$ ($3.8 \times 10^{-4}$ M) and expressed in w/w (g/g), interferent/cyanide. The effect of $SO_4^{2-}$, $Cl^-$, $NO_3^-$, $F^-$, $CH_3COO^-$, $PO_4^{3-}$ and metal ions in the presence of cyanide was also examined. Aliquots (10 mL) of $1.0 \times 10^{-2}$ M aqueous solutions of these ions were mixed with $10\,\mu g\,mL^{-1}$ ($3.8 \times 10^{-4}$ M) portion of cyanide solution and the mixtures were distilled in the presence of 1:1 $H_2SO_4$ followed by measuring the cyanide by reaction with cobalt (II) phthalocyanine tetracarboxylate reagent as described above. No effect was caused by 1000-fold excess of these ions.

### 2.6 *Determination of cyanide in electroplating wastewater*

Acid digestion of electroplating wastewater samples was carried out according to the standard methods for the examination of water and wastewater [32]. A 10 mL aliquot of the electroplating wastewater was transferred to the cyanide distillation equipment, diluted to 50 mL with 1:1 $H_2SO_4$ followed by distillation. The liberated HCN was collected in 20 mL of 1 M NaOH scrubbing solution containing 50 mg of $PbCO_3$. The solution was diluted in 100-mL volumetric flask with deionised distilled water. The cyanide concentration was measured spectrophotometrically as described above.



## 3. Results and discussion

### 3.1 *Nature of the reaction*

Metallo-phthalocyanines exhibit monomer/dimer equilibrium (Figure 1). The dimer form, most probably, involves metal-metal binding as confirmed in other similar metallo-porphyrins [34]. Interaction of cyanide with these compounds in dimethylsulphoxide media involves axial ligand coordination [35,36]. In this work, cobalt (II) phthalocyanine tetracarboxylate was prepared and its absorption spectrum was measured in aqueous media. The spectrum of the reagent exhibits a sharp absorption maximum at 615 nm due to a dimer form and a broad inflection break at 666–670 nm due to the monomer form. Upon addition of cyanide ion, the intensity of the dimer peak slightly decreases and the absorption intensity of the monomer peak undergoes a significant increase ($\varepsilon = 7.7 \times 10^4\,L\,mol^{-1}cm^{-1}$) with a bathochromic shift to 682 nm (Figure 2). The increase in the absorption is linearly related to cyanide concentration. It has been reported that metallo-phthalocyanine derivatives display a monomer peak at 670–690 nm and a dimer peak at 636 nm [37]. Thus, the conversion of the dimer form of metallo-phthalocyanines into the monomer one is associated with a bathochromic shift.

The effect of pH on the proposed reaction was tested by adjusting different cyanide test solutions to pH 4–11 with dilute NaOH and/or $H_2SO_4$ prior to the addition of the reagent. No significant difference in the absorbance of these solutions over this wide pH range was noticed. The effect of the reagent concentration on the reaction was also investigated. As the reagent concentration decreased (down to $5\,\mu g\,mL^{-1}$), the absorbance values decreased and the sensitivity decreased. Higher reagent concentration ($>30\,\mu g\,mL^{-1}$) was associated with non linear high absorbance values. The optimum reagent concentration which falls within the linear calibration range and used for measuring up to $15\,\mu g\,mL^{-1}$ ($5.8 \times 10^{-4}$ M) cyanide was $20\,\mu g\,mL^{-1}$. Under the optimised conditions, Beer's law is

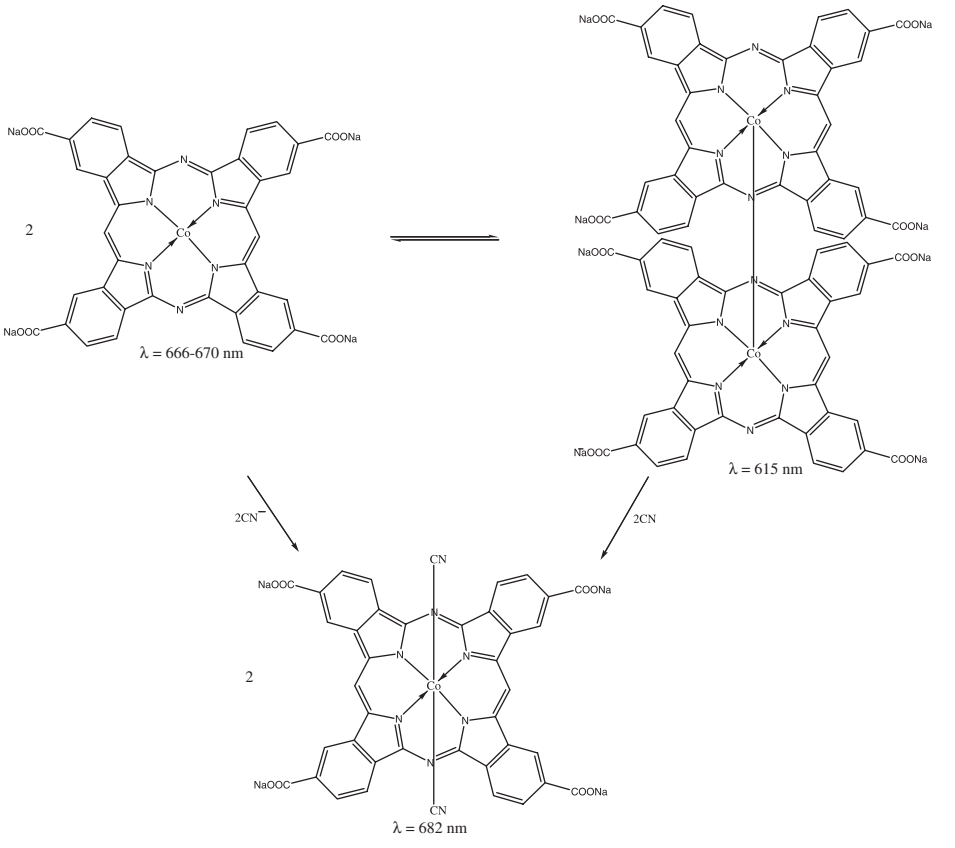


Figure 1. Axial ligation of Co (II) phthalocyanine tetracarboxylate by cyanide ion.



obeyed over the range 0.15 to 15 $\mu g\,mL^{-1}$ ($5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M) cyanide, with a correlation coefficient of 0.9998. The linear calibration curve is described by Equation (2):

$$\Delta A = (0.0011 \pm 0.0001) + (0.0416 \pm 0.0001)\left[CN^{-}, \mu g\ mL^{-1}\right] \quad (2)$$

The detection limit was calculated according to IUPAC guidelines [38]: $LOD = K\,S_o/S$, where $S_o$ is the standard deviation of the blank measurement ($n = 6$), $S$ is the slope of the calibration curve and $K$ is a numerical factor depending on the degree of confidence level needed. With $K = 3$ (i.e. 3 $S_o$) the detection limit is 0.025 $\mu g\,mL^{-1}$ (the relative standard deviation measured over cyanide concentration of 0.5–15 $\mu g\,mL^{-1}$ ($1.9 \times 10^{-5}$–$5.8 \times 10^{-4}$ M) is ±0.7% ($n = 5$), and Sandell's sensitivity (i.e. cyanide concentration equivalent to 0.001 absorbance unit) [39] is $4.3 \times 10^{-3}$ $\mu g\,cm^{-2}$. The colour reaction took a few seconds and was stable for at least 8 hours without any noticeable deterioration.

The stoichiometry of the reaction of Co (II) phthalocyanine tetracarboxylate with cyanide was examined using the continuous variations Job's method [40], a 1 : 2 molar was found. The formation constant of $CN^-$/Co (II) phthalocyanine tetracarboxylate complex was measured from the plot of log $[(A_x - A_o)/(A_\infty - A_x)]$ against log $[CN^-]$ [29,34], where the $y$-intercept of the extrapolated linear relation indicates the logarithm of the stability

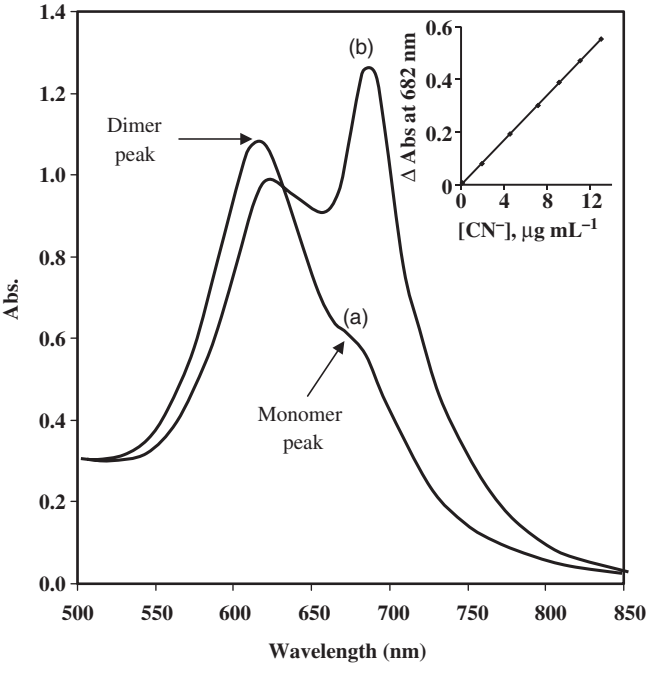


Figure 2. Absorption spectra of Co (II) phthalocyanine tetracarboxylate chromogen in the absence (a) and presence (b) of $15\,\mu g\,mL^{-1}$ ($5.8 \times 10^{-4}$ M) cyanide standard solution, and the cyanide calibration curve (insert).

constant of the cyanide complex. The formation constant ($K_f$) measured from the spectrophotometric data at $25 \pm 0.1^{\circ}C$ was calculated and found to be $5.4 \pm 0.01 \times 10^6$.

### 3.2 *Method assessment*

Replicate measurements ($n = 10$) of $2.00\,\mu g\,mL^{-1}$ ($7.7 \times 10^{-5}$ M) internal quality control aqueous cyanide sample (IQS) and calculation of the student's ($t$) values at 95% confidence level were made.

$$t_{exp} = \frac{|\mu - \overline{X}| \times \sqrt{n}}{s} \tag{3}$$

where $\mu$ is the concentration of the internal quality control sample, $X$ is the average concentration found, $n$ is the number of replicate analysis and $s$ is the standard deviation of the measurements. No statistical difference was detected between the practically obtained ($t_{exp} = 0.898$) and the theoretically tabulated ($t = 1.812$) values at $n = 9$ and $\alpha$ 0.05; thus the null hypothesis is retained. The mean recovery obtained by spiking of $0.50\,\mu g\,mL^{-1}$ ($1.9 \times 10^{-5}$ M) internal quality control aqueous cyanide sample to $2.00\,\mu g\,mL^{-1}$ ($7.7 \times 10^{-5}$ M) cyanide test solution is $98.6 \pm 0.9\%$. This confirms the applicability of the method for accurate routine analysis of cyanide ion in various industrial wastewaters. Based on duplicate measurements of the cyanide internal quality samples for 10 days, control charts ($\overline{X}$ and $R$) confirm that the obtained data are under statistical control (Figure 3) [41].

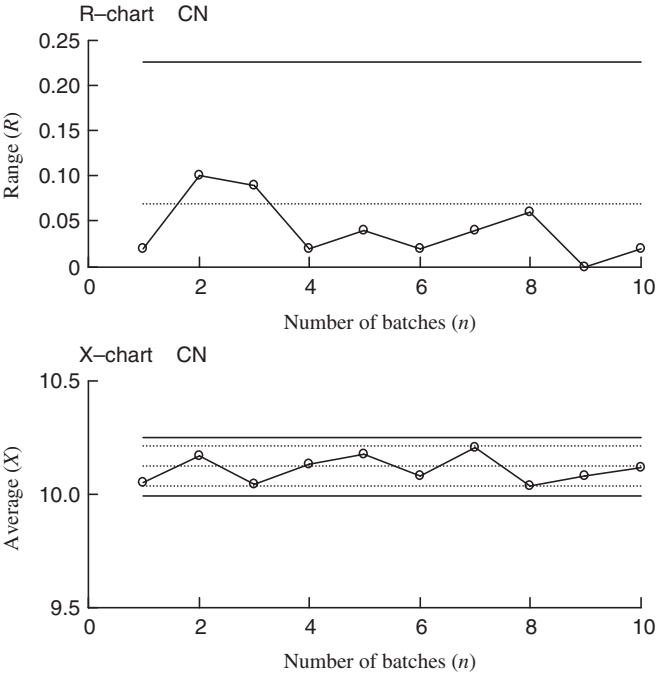


Figure 3. Control $X$ (average) and $R$ (difference) charts.



Validation of the proposed spectrophotometric method was performed using the quality assurance standards [42]. Six batches (six determinations each) covering the concentration range of 0.15–15.0 $\mu g\,mL^{-1}$ ($5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M) of cyanide were used for evaluation of the range, accuracy, trueness, precision, lower limit of detection, standard deviation, within-day repeatability ($CV_w$) and between-day-variability ($CV_b$). The results obtained (Table 1) revealed a short reaction time (10 s), reagent stability (8 months), minimal manipulation steps (a single reagent), wide range of linear response (0.15–15 $\mu g\,mL^{-1}$; $5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M cyanide) over an extended pH range (pH 4–11), low detection limit (20 $ng\,mL^{-1}$; $7.7 \times 10^{-7}$ M), high accuracy (98.6%) and good precision (0.5%).

### 3.3 *Tolerance of volatile acid releasing anions*

Methods used for determining cyanide in electroplating wastewater commonly involve a prior acid distillation step to break down the metal complexes, and release of hydrocyanic acid followed by measurement using a variety of techniques. Thus, volatile acid releasing ions are expected to release volatile gases during the acid distillation step and collected with the cyanide in the receiving alkaline scrubber. In this study, the tolerance of different volatile acid releasing anions (e.g. $CH_3COO^-$, $N_3^-$, $NO_2^-$, $S^{2-}$, and $SO_3^{2-}$) was examined. Concentration level of $CH_3COO^-$, $N_3^-$, $NO_2^-$, and $S^{2-}$ up to $1.0 \times 10^{-2}$ M had no effect on the absorbance of the chromogen compared to the blank. Common anions which are present in the electroplating baths or not easily converted into volatile species during distillation (e.g. thiocyanate, iodide, chloride, bromide) were not tested. On the other hand, the reaction of $SO_3^{2-}$ with the chromogenic reagent displays a strong absorbance

Table 1. Performance characteristics of the spectrophotometric assay method of determining cyanide using cobalt (II) phthalocyanine tetracarboxylate chromogenic reagent.

| Parameters | Value* |
|---|---|
| Measurement wavelength, $\lambda_{max}$ (nm) | 682 |
| Molar absorptivity, $\varepsilon$ l mol$^{-1}$ cm$^{-1}$ | $7.7 \times 10^4$ |
| pH range of measurement, pH | 4–11 |
| The detection limit LOD, ng mL$^{-1}$ | 20 ($7.7 \times 10^{-7}$ M) |
| Linear range, μg mL$^{-1}$ | 0.15–15.0 ($5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M) |
| Correlation coefficient, $r$ | 0.9998 |
| Sandell's sensitivity, μg cm$^{-2}$ | $4.3 \times 10^{-3}$ |
| Accuracy, % | 98.6 |
| Trueness, % | 98.7 |
| Precision, $\sigma$% | ±0.5 |
| Relative standard deviation, % | ±0.7 |
| Within-day repeatability, $CV_w$ % | ±0.6 |
| Between-day reproducibility, $CV_b$ % | ±0.8 |

Note: *Based on 6 measurements.



close to that of the same concentration of the cyanide. Measurement of equimolar concentration of $CN^-$ and $SO_3^{2-}$ ions shows a positive interference probably due to the strong interaction of $SO_3^{2-}$ ion with the chromogen. The tolerance concentration of sulphite is less than 3-fold the cyanide.

Although $SO_3^{2-}$ is seldom present with $CN^-$ in wastewater of electroplating baths, the formation constant of Co (II) phthalocyanine tetracarboxylate/sulphite complex was measured and found to be close to that of $CN^-$ ($K_f = 1.3 \pm 0.01 \times 10^6$ at $25 \pm 0.1$°C). However, the effect of $SO_3^{2-}$ was circumvented by addition of $PbCO_3$ (50 mg) to the alkaline scrubbing solution. $PbCO_3$ reacts with $SO_3^{2-}$ and $S^{2-}$, if present, to give insoluble lead salts without affecting the cyanide assay [32]. Metal ions (e.g., $Fe^{3+}$, $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Ag^+$, $Au^{3+}$, $Cr^{3+}$, $Zn^{2+}$) at concentration as high as 1000-fold excess over cyanide have no adverse effect on the sensitivity of the method, because the acid distillation step liberated cyanide, which was collected as a pure alkaline cyanide solution leaving the metal salts behind in the distillation flask as residues. In the absence of metal and sulphite ions, the cyanide ion can be directly determined without a prior distillation.

### 3.4 *Determination of cyanide in electroplating wastewater*

Most of the cyanides in electroplating wastewaters exist as rinse waters, spillage and drippings from the metal plating solutions which present in the form of stable metal-cyanide complexes. Prior separation of HCN, by acid distillation or membrane diffusion followed by collection and measurement, is a common approach recommended by the United States Environmental Protection Agency, USEPA [43], International Standardization Organization, ISO [44], American Society for Testing and Materials, ASTM [45], and American Public Health Association, APHA [32]. Different electroplating wastewater solutions were collected, subjected to acid distilled and the hydrocynic acid was absorbed in alkaline solution and spectrophotometrically assessed by the

Table 2. Determination of cyanide in electroplating wastewater using spectrophotometry with cobalt (II) phthalocyanine tetracarboxylate chromogen and potentiometry with a cyanide ion selective electrode.

| Wastewater** | Cyanide content, ($mg\,L^{-1}$)* | | Relative error, % |
|---|---|---|---|
| | Spectrophotometry (cobalt phthalocyanine-tetracarboxylate) | Potentiometry (solid-state cyanide electrode) | |
| Gold electroplating bath (1) | $225.7 \pm 0.6$ ($8.68 \times 10^{-3}$ M) | $221.4 \pm .0.8$ ($8.51 \times 10^{-3}$ M) | +1.9 |
| Gold electroplating bath (2) | $88.4 \pm 1.4$ ($3.40 \times 10^{-3}$M) | $90.1 \pm 1.3$ ($3.47 \times 10^{-3}$M) | −1.9 |
| Gold electroplating bath (3) | $32.1 \pm 1.2$ ($1.23 \times 10^{-3}$ M) | $31.7 \pm 1.1$ ($1.22 \times 10^{-3}$ M) | +1.3 |
| Silver electroplating bath (1) | $178.8 \pm 1.4$ ($6.87 \times 10^{-3}$ M) | $181.4 \pm 1.6$ ($6.97 \times 10^{-3}$ M) | −1.4 |
| Silver electroplating bath (2) | $65.9 \pm 1.2$ ($2.53 \times 10^{-3}$ M) | $67.7 \pm 1.2$ ($2.60 \times 10^{-3}$ M) | −2.7 |
| Silver electroplating bath (3) | $116.4 \pm 1.4$ ($4.47 \times 10^{-3}$ M) | $115.1 \pm 1.2$ ($4.43 \times 10^{-3}$ M) | +1.3 |
| Chromium electroplating bath (1) | $71.7 \pm 1.1$ ($2.76 \times 10^{-3}$ M) | $69.8 \pm 1.2$ ($2.58 \times 10^{-3}$ M) | +2.7 |
| Chromium electroplating bath (2) | $18.2 \pm 1.9$ ($7.00 \times 10^{-4}$ M) | $17.9 \pm 2.2$ ($6.88 \times 10^{-4}$ M) | +1.7 |

Notes: *Average of 5 measurements.
**The main composition of $Au^{3+}$, $Ag^{+}$ and $Cr^{3+}$, electroplating baths are: $Au^{3+}/CN^{-}/OH^{-}$, $Ag^{+}/CN^{-}$, and $CrO_3/SO_4^{2-}/CN^{-}$, respectively.



proposed method. A comparison of the data with potentiometric results obtained using a solid-state cyanide ion selective electrode showed an agreement within ±2.7% (Table 2). The *F* test revealed no significant difference between the means and variances of the two set of results. Found and tabulated *F* values are 1.86 and 3.44, respectively.

## 4. Conclusions

Co (II) phthalocyanine tetracarboxylate has been prepared as a novel water soluble chromogen for spectrophotometric determination of cyanide ion. The reagent forms a stable 1 : 2 complex with cyanide {[Co (II) Pc-COOH]: [2 CN]} ($K_f = 5.4 \pm 0.01 \times 10^6$) at $25 \pm 0.1$°C. At 682 nm, the Beer's law is obeyed over cyanide concentration of 0.15–15 $\mu g\,mL^{-1}$ ($5.8 \times 10^{-6}$–$5.8 \times 10^{-4}$ M), the lower detection limit is 0.02 $\mu g\,mL^{-1}$ ($7.7 \times 10^{-7}$ M) and the colour is stable over the pH 4–11. Cyanide in electroplating wastewater samples was measured by prior distillation with $H_2SO_4$ to release HCN, absorption in sodium hydroxide scrubber followed by reaction with the reagent. The results agreed fairly well with data obtained by potentiometry using a cyanide ion selective electrode. No interference was caused by $SO_4^{2-}$, $Cl^{-}$, $N_3^{-}$, $NO_2^{-}$, $NO_3^{-}$, $F^{-}$, $CH_3COO^{-}$, $PO_4^{3-}$, $S^{2-}$ and metal cations. The present cyanide assay method displayed several advantages over many of those previously suggested using spectrophotometry [17,19,20,46–50].

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