Available online at http://www.journalijdr.com

International Journal of
DEVELOPMENT RESEARCH

ISSN: 2230-9926

IJDR

International Journal of Development Research
Vol. 05, Issue, 08, pp. 5186-5190, August, 2015

Full Length Research Article

STUDY ON CYANIDE DETERMINATION BY PYRIDINE – PYRAZOLE REAGENT AND ITS APPLICATION TO EVALUATE SOME CYANIDE CONTAMINATED WASTEWATER RESOURCES IN HANOI

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ARTICLE INFO

Article History:
Received 30th May, 2015
Received in revised form
12th June, 2015
Accepted 27th July, 2015
Published online 31th August, 2015

Key Words:
Cyanide, Pyridine – Pyrazolone Reagent,
Spectrometric Method,
Evaluation Method.

ABSTRACT

The Cyanide compounds have been listed as one of the toxic pollutants that are usually released into environment. A study on cyanide analysis has been devised to determine the total cyanide concentration in wastewater. This work determines the concentration of total cyanide in water and wastewater collected in some metal plating factories in Hanoi. The determination of cyanide (simple CN^-) is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine – pyrazolone to form a stable color complex. Therefore, before chlorination of cyanide, the all cyanide compounds present in samples must be broken down by an acid reflux and distillation. The cyanide distillation also removes certain interferences from water samples. The cyanide concentration in the samples was determined by measuring absorbance at λ_{max} = 614 nm in a suitable experimental condition such as solution pH = 6.87, chloramine -T volume = 0.5 mL, pyridine – pyrazalone reagent solution = 3.0 mL, the complex forming time = 20 min. The LOD and LOQ of the method were established being 5.1×10^{-3} mg/L, 0.017 mg/L respectively. The method was applied to determine cyanide in wastewater of some metal plating factries in Hanoi, Vietnam.

INTRODUCTION

Cyanide compounds have been widely used as an essential raw material in industries including textile, plastics, paints, photography, electroplating, agriculture, medicine and metallurgy (Terry *et al.* ; ATSDR.1993, Asell *et al*., 1970). Cyanide compounds have been listed as one of the toxic pollutants that are usually released into environment. Humans are in close contact with cyanide in their daily life through food, drink, smoking, medicines or using products which contain cyanide (Chandra *et al,* 1980; Blanc *et al*, 1985; Fiskel *et al.,* 1981). Cyanide does not accumulate in the body and does not cause chronic diseases, but because of its ability to bind iron in blood by forming complexes, it can inhibit oxygen transfer to the cells, thereby causing suffocation of humans and animals (Hibbs *et al.,*1979). Liquid or gaseous hydrogen cyanide and alkali salts of cyanide can enter the body through inhalation and ingestion or absorption through the eyes, skin (Borowitz *et al*). The toxicity of cyanide is typically expressed by the dose that is lethal to 50% of the exposed population (LC50 or LD50). For example, the LD50 for cyanide ingestion is 50–200 mg, or 1–3 mg/kg of body weight, calculated as hydrogen cyanide (Cyanide Health Effects, U.S.Environmental Protection Agency Washington). Due to the high toxicity of cyanide, the cyanide present in environment, mainly in water or wastewater must be examined before use or discharging to water body. Besides, the determination of total cyanide concentration is very important problem for cyanide contaminated water resource treatment. Methods determining cyanide present in water can be classified into three categories including total cyanide, available or weak acid dissociable cyanide and free cyanide. There are many suitable techniques to determine every kind of cyanide compounds (Mohammad Sarwar *et al*, 1996; APH (2012), USEPA (1996), Lindsay *et al,* 2004). In this work, the total cyanide concentration in water sample was determined by spetrophotometric method based on post- distillation samples and followed colorimetric reaction involving chloramine –T and pyridine – pyrazolone. All factors influencing on the colorimetric reaction were examined. An application of this method to determine cyanide in wastewater collected from some metal eletroplating factories in Hanoi has been carried out.

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MATERIALS AND METHOD

Materials

Chloramine –T, (1%)

Dissolve 1.0 g chloramine – T ($C_7H_7ClNNaO_2S.3H_2O$) in 100 mL distillated water. This solution is unstable and must be prepared immediately before use.

Cyanide standard solution, 1000 mg/L; 100 mg/L; 10 mg/L

The stock cyanide solution of 1000 mg/L was prepared by 1.885 g NaCN dissolving in 1000 mL distillated water. The cyanide solutions of 100, 10 mg/L were prepared from this solution.

Pyridine-pyrazole reagent solution

- *Pyrazolone solution saturated*: add 0.25 g 3-metyl-1-phenyl-2-pyrazolin-5-one to 50 mL distillated water at room temperature, with stirring and filter.
- *Bis- pyrazolone*: add 0.01 g bis- pyrazolone (3,3'-dimetyl-1,1'-diphenyl-(4,4'-bi-2-pyrazolin)-5,5'-dione) in 10 mL pyridine (C_5H_5N) and filter..
- *Mix two above solutions together with stirring*. The mixed reagent develops a pink color does not affect color development of cyanide. Prepare this reagent fresh daily or before each use.

Lead acetate solution $(CH_3COO)_2$ Pb 0.08 M: prepared from lead acetate salt, analytical pure

Sodium phosphate buffer 1M (pH 5.8 – 8.0)

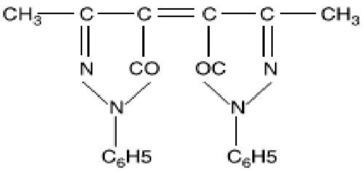
- Dissovle 12g NaH_2PO_4 in distillated water and make a final volume of 100 mL.
- Dissolve 14.2g Na_2HPO_4 in distillated water and make a final volume of 100 mL.
- Mix two buffers in certain ratio to abtain the disigned pH.

NaOH, HCl solutions with different concentrations used for adjusting pH

Experimental procedure

Colormetric procedure of determination of cyanide in water sample by pyridine – pyrazolone

The principle of experimental procedure is based on the conversion of CN^- into CNCl at pH < 8 without hydrolyzing to the cyanate by the reaction with the chloramine – T which acts as a source of hypochlorous (HOCl). After the reaction is complete, the CNCl forms a blue dye (pyrazole blue) on the addition of the pyridine – pyrazolone reagent. The pyrazole blue chemical structure is presented in the work (Taylor and Francis Group):



Pyrazole-blue

The experimental procedure was carried out as follows

Take 50 mL- flask, add 5 mL cyanide sample to flask, then 0.5 mL chloramine – T, shake and rest 3 min. Add in flask 5 mL buffer and 3 ml pyridine – pyrazolone and shake. Add distilled water in flask to reach to 50 mL. All 20 min for the reaction to proceed. The absorbance of sample and blank sample (without CN^-) was measured at the optimal wave length of 614 nm with the UV- Vis Biochrom Libra S60 spetrophometer.

Cyanide distillation procedure (cyanide in waste water)

The cyanide distillation was carried out using a reflux distillation apparatus assembled as shown in Fig.1. Place a suitable sample volume in the boiling flask. Connect the boiling flask, condenser, absorber and vacuum pump and control if the apparatus works well. Slowly add 25 mL 18 N sulfuric acid through the funnel. Heat the solution to boiling. Reflux for one house. Turn off the heat and continue the airflow for least 15 min. After cooling the boiling flask, disconnect the absorber and close off the vacuum pump. Drain the solution from the absorber into a volumetric flask. Wash the absorber with distillated water, and add the washings to the flask. Dilute to volume with distillated water. The obtained sample solution is used for cyanide determination as suggested above method.

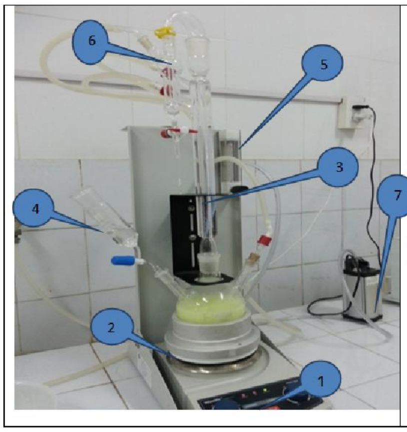


Fig. 1. Cyanude distillation train

1. Electric heater
2. 500 mL- boiling flask
3. Water cooled condenser
. Fennel for H_2SO_4.
5. flowmeter
6. absorption vase with NaOH
7. Vacuum pump MVP200.

Fig.1. Cyanide distillation apparatus

Sampling (the wastewater sampling sites were some places of metal plating in Thanh Tri, Hanoi). Wastewater sampling were carried out in two different times in several sites of Thanh Tri plants. Three wastewater samples (noted M1, M2, and M3) were collected in the distance of 100 and 500 m from the point of discharge of the metal plating plant effluent. Three samples (M4, M 5, and M6) were collected in the distance of 300m and 1500m from the point of discharge of metal finishing plant effluent. The four samples (M7, M8, M9, and M10) were collected in a lock plant. Each sample was collected in polyethylene bottle which has been previously washed, rinsed thoroughly with distilled water and dried. The water samples are preserved at the time of collection with NaOH to a pH ≥12 and were transported to the laboratory in an ice bag. The samples were preserved in refrigerator in the laboratory where they were analyzed within two weeks days after the time of collection. Before distillation, the sample needs to filter to remove suspense.

RESULTS AND DISCUSSION

Plot of calibration

Uv- spectrogram of pyrazole blue

The uv- spectrograms pyrazole blue of samples contained 0.10 mg/L CN^- are presented in Fig.3.1**.**

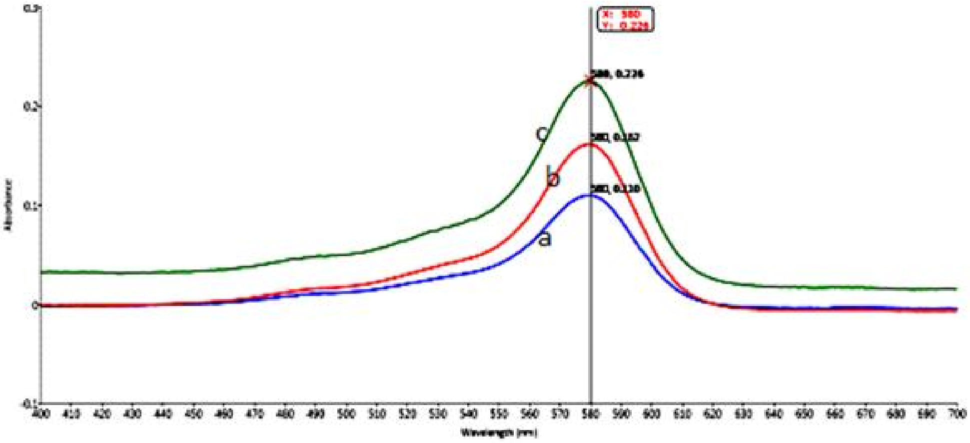


Fig.3.1. UV- pyrazole blue spectrograms with different concentration of CN^-: a. CN^- = 0.04 mg/L; b. CN^- = 0.06 mg/L; c. CN^- = 0.08 mg/L.

The experimental data showed that the maximum absorbance (peak) appeared at λ_{max} = 614 nm and the peak height increases with increasing CN^- concentrations. The λ_{max} = 614 nm was used for the further measurements**.**

Determination of optimal coditions for pyrazole blue

a. *Determination of optimal pH*: The solution pH were varied from 4.0 to 8.5 by using the phosphate buffer. The experimental data are present in Fig. 3.2.

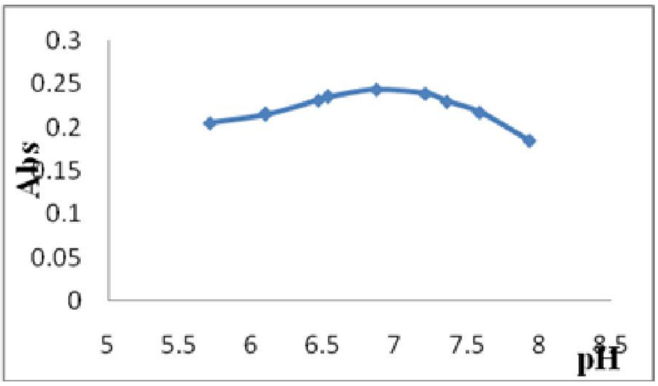
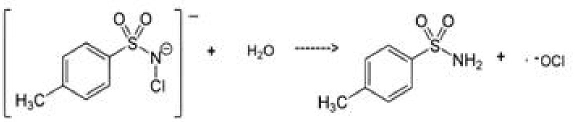


Fig.3.2. Dependence of absorbance on pH in the range from 6.53 to 736

The obtained data showed that the pH = 6.87 was selected for the futher experiments.

b. *Determination of optimal chloramine – T amount*: The dosage of chloramine – T amount used is very important in the cyanide chlorination process. Chloramine –T is considered as the source releasing ClO^- to oxidize CN^-. The formation of ClO^- may be present in the reaction as follows:



The cyanide oxidation process can take place in two steps as follows:

$$NaCN + NaOCl = NaCNO + NaCl \qquad \ldots\ldots(1)$$
$$2NaCNO + 3NaOCl + H2O = NaCl + N_2 + 2NaHCO_3 \qquad \ldots\ldots(2)$$

For determination of CN^- concentration in water samples, the cyanide oxidation must be stop in the reaction (1). It means the added chloramine -T to producing NaOCl must be sufficient, enough to do not have the reation (2), causing CN^- lost. This fact is fitted to the experimental data present in Fig. 3.3, when the dependence of absorbance of pyrazole blue on chloramine – T was examined.

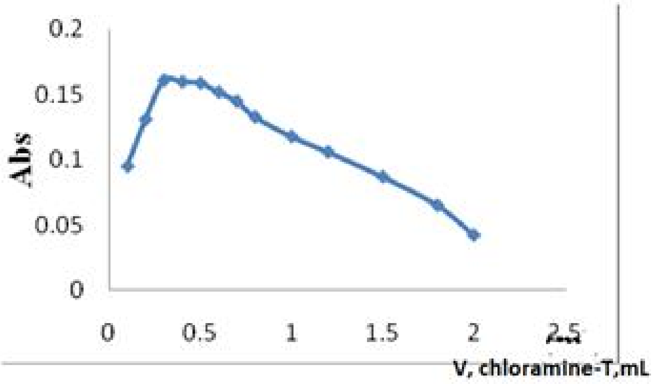


Fig. 3.3. Dependence of absorbance on V, chloramine – T

From this experimental data, V,chloramine – T being 0.5 mL was selected for the further experiments.

c. The dependence of pyrazole blue absorbance on pyridine-pyrazoline reagent

The pyridine-pyrazoline reagent amount influencing on the absorbane is presented in Fig. 3.4.

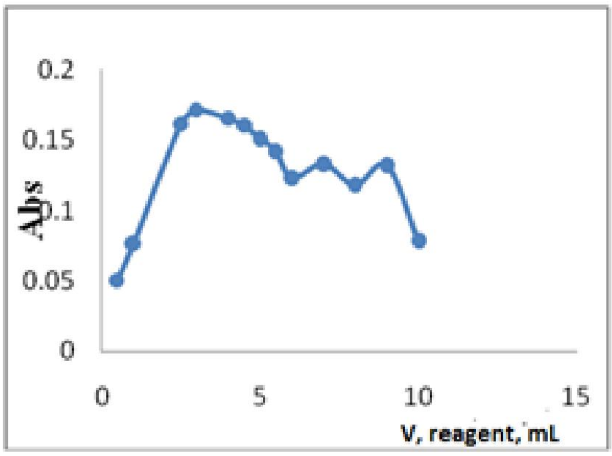


Fig.3.4. Dependence of absorbance on V, chloramine – T

The V- pyridine-pyrazolonevolume being 3.0 mL corresponding to the maximum absorbance was selected for the further experiments. When the V- pyridine-pyrazolone higher than 3.0 mL, the absorbance decreases. It may be due to the slow decomposition of the pyrazole blue to form other compounds.

d. Influence of ti me on color stability of pyrazole blue: The experimental data (not seen here) showed that the pyrazole blue is stable in 20 min.

Calibration curve

Using the obtained optimal experimental conditions, the calibration curve of the absorbance depending on the cyanide concentrations was established and present in Fig. 3.5 and the regression equation corresponding to the plot is : $A = 1.6973xC_{CN-} + 0.0049$; with $R^2 = 0.9984$.

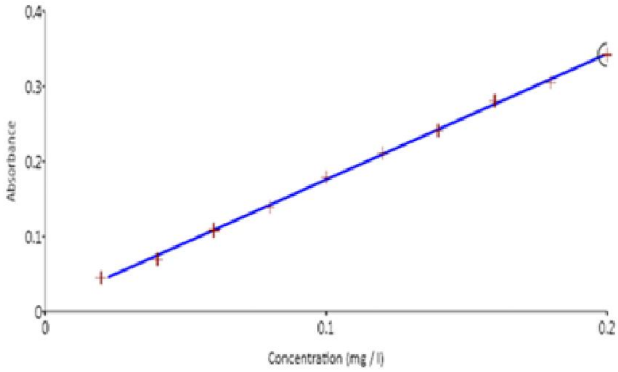


Fig.3.5. Calibration curve of the CN^- concetrations

Determination of the Limit of Detection (LOD) and Limit of Quantification (LOQ)

The experimemts were carried out with 10 samples in which CN^- concentration is 2 mg/L. The experiments were also carried out in the optimal condition. From the obtained absorbance corresponding to each sample, the standard deviation (s), LOD, LOQ were determined and thet are as follows:

$$S = \sqrt{\frac{\sum(A_i - \overline{A})^2}{n-1}} = 0.0017; \quad = \quad \overline{A} = 0.023$$

$$LOD = 3 \times S = 3 \times 0.0017 = 5.1 \times 10^{-3} \text{ (mg/L).}$$

LOQ = 10xS = 10x0.0017 = 0.017 (mg/L)

Determination of cyanide in wastewater

The cyanide concentrations of wastewater collected from the metal plating factories in Thanh Tri, Hanoi in two different periods are presented in Fig. 3.6, 3.7.

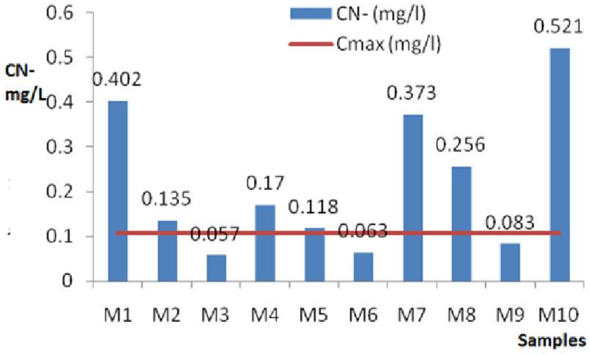


Fig.3.6. The cyanide concentration in wastewater (first period)

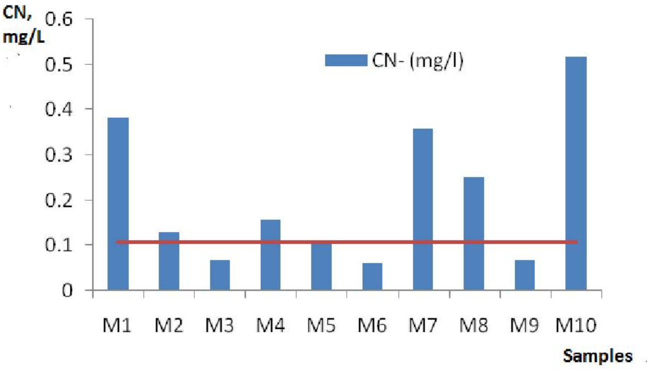


Fig. 3.7. The cyanide concentration in wastewater (scond piriod)

The experimental data showed that Samples M1, M2, M4, M7, M8 and M10 having cyanide concentrations exceeded the permitted criteria.The wastewater resources corresponding to these samples must be treated prior allowing to discharge to environment

Conclusions

The cyanide compounds present in wastewater have been listed as one of the toxic pollutants that are usally released into environment. Therefore cyanide compounds present in all wastewater must be controlled and treated prior allowing to discharge into environment. The cyanide compounds can be analysed by a lot of methods. Here, determination of cyanide compounds by the spectrophotometric method using pyridine – pyrirazole has been studied in detail. After cyanide chlorination with chloraminte -T, the reaction product forms a color compound with pyridine – pyrazolone that was been used for analyzing cyanide present in water sample based on measurement of absorbence. The optimal experimental conditions of this method have been determined. A calibration plot for cyanide determination has been established. An application of this method to analyzing cyanide compounds present in wastewater of some metal plating factories in Thanh Tri Hanoi has been successfully suggested.

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