2. Have assessed the ability to decompound the stable cyanides complex (take 2 iron complexes of the $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ represented) with cyanide distillation system in acidic medium.

- Performance of decomposition to 84 ÷ 100%.
- The average recovery of the complex on range of 90÷ 100% consistent with the provisions of AOAC.

3. By applying the method to analyze 1320 wastewater samples at 44 locations in 4 districts of Hanoi and 180 wastewater samples at 6 position of 2 gold mining places in Thai Nguyen province in both rainy and dry seasons. The obtained results showed that:

• For metal plating waste water in Hanoi:

- The average cyanide content of 04 districts are relatively high (~ 2,150 mg/L), excess of criteria B 40: 2011 / BTNMT about 20 times, of which 52.3% of the samples exceeded the wastewater QCVN industry.
- The average concentration of cyanide in water samples in dry season higher than in the wet season about 21.2%, and cyanide in a some samples are negligible

• For waste water of gold mining dumps in Thai Nguyen:

- The average content of cyanide in waste water of 02 of gold mining dumps is relatively high (0.571 mg/L). Compared to the B of criteria 40: 2011/BTNMT exceed 5.3 times, which has 88.9% of the samples exceed QCVN 40: 2011/BTNMT. If compared with the Criteria B, QCVN 08: 2008/BTNMT exceed 28.5 times.
- The average concentration of cyanide in water samples dry season higher than the wet season about 10%.

Thus, cyanide contamination levels are very serious.

4. Has the study of factors affecting the oxidation of cyanide in waste water treatment metalized by agent $Na_2S_2O_5$ / Cu^{2+} at laboratory scale. Results of wastewater treatment facility in a number of villages in metal plating Thanh Thuy and galvanizing facility Hai Boi commune, Dong Anh District, Hanoi have reached 98.52% and Performance 99.43%.

5. Along with chemical methods, has researched cyanide in waste water treatment galvanized metal, water hyacinth, results showed:

- Just 1kg of hyacinth after 28 days, the treated effluent is 36 liters (0.190 mgCN- concentration/L) standard level of criteria B, QCVN 08: 2008 /BTNMT.
- The average age hyacinth better handle young hyacinth.

INTRODUCTION

1.The urgency of the subject

In our country the problem of pollution of water sources in many places are at an alarming rate, especially in the big cities and industrial zones. Speed of industrialization and urbanization was accelerated with the increase of population by waste sources, has caused increasingly heavy pressure on social and community. In wastewater, wastewater containing cyanide group is particularly interested because of its toxicity, because cyanide is classified as hazardous waste. Acid HCN and its salts are very strong poison, with just 50 mg it can kill a person. However, the cyanide salts were used extensively in industries such as industrial plating (gold, silver, copper, zinc ...), gold mining industry, industry manufacturing pigments (pigment) used for paint, powder paint, and textile dyeing. Beside, cyanide salts were as raw materials manufacturing pesticide as calcium cyanide to kill bed bugs and insects in housing. Now there are many methods of cyanide analysis such as ion chromatography, capillary electrophoresis chromatography, electrochemistry However, these methods are highly sensitive, high accuracy, but must use equipments expensive and often only equipped in laboratories at large. Spectrophotometric method requires only a simple optical measuring machine and inexpensive reagents. Spectrophotometric method UV-Vis based on pyridine - pyrazolone or pyridine - barbituric reagents determining cyanide were suggested by the authors but not being studied in detail.

Therefore, the theme *"Research and analysis to determine the amount and treatment of cyanide in wastewater by chemical methods and biological"* was chosen to be our doctorial dissertation title.

2. The aim of the thesis

• Developing method to determine cyanide:

The thesis was focused on building spectrophotometric method UV-Vis to analyze the concentration of cyanide in the water, using reagents: pyridine - pyrazolone and pyridine - barbituric. On that basis, by comparing, evaluating between them, the appropriate method will be selected.

• Determination of cyanide in water samples:

Applying the method developed, determining the concentrations of cyanide in waste water samples of the metal plating places (in 04 districts of Hanoi such as in Thanh Tri, Phuc Tho, Thanh Oai and Dong Anh Eastern) and water samples from gold mining waste (in 02 gold mining places as Ngan Me and My Hoa Dong Hy district, Thai Nguyen

province). From the data obtained, allowing an overall rating cyanide pollution levels in these areas.

• Studying two cyanide processing methods in laboratory scale: chemical method: using oxidizing agent $Na_2S_2O_5$ combined catalyst Cu^{2+}; Biological methods: using water hyacinth plants.

3. Research Content

- Investigation of optimal conditions and building spectrophotometric calibration curve to determine the amount of cyanide using pyridine - pyrazolone and reagents pyridine – barbituric reagents
- Assess the efficiency of cyanide conversion in stable complexes with the distillation system dedicated cyanide.
- Sampling and analysis systematically cyanide concentration in the wastewater samples. Based on the analytical results in 03 years (2013-2015) in both dry and rainy seasons, a comprehensive assessment of cyanide pollution levels in these localities was implemented.

Research and select oxidizing agent sodium metabisulfite combined catalyst ($Na_2S_2O_5$ and Cu^{2+}) and hyacinth plants to handle cyanide in some typical water samples at laboratory scale.

4. The contributions of the thesis

- Systematically study to find the optimal conditions for the reaction of cyanide compoundation with 2 color reagents: pyridine - pyrazolone and pyridine – barbituric was implemented. The optimal absorption of the cyanide compounds with reagents and the standard curve with high accuracy to determine cyanide have been established.
- A comprehensive study to confirm the value of use of the method such as the limit of detection, LOD, LOQ limit of quantification, repeatability, precision, thereby confirming the reliability of the method.
- Detailed analysis results in 3 years (2013-2015) being a dataset allows a comprehensive assessment of the current state of cyanide in waste water pollution in metal plating in 4 districts of Hanoi (in 44 locations, 1320 samples /3 years) and in wastewater of 2 places of gold mining in Thai Nguyen (in 6 positions, 180 samples /3 years). The results showed that the cyanide pollution in the locality is very serious.
- Used $Na_2S_2O_5$ combined catalyst of Cu^{2+} and hyacinth plants to handle cyanide in the waste water are the methods having high processing performance.

6. The layout of the thesis

The thesis consists of 145 pages, with 63 tables and 52 figures, the structure consists of: Introduction 04 pages; Chapter 1: Overview 36 pages; Chapter 2: Experimental 31 pages; Chapter 3: Results and discussion 65 pages; Conclusion 02 pages; The list of works of authors related to the thesis 01 pages; Reference page 06.

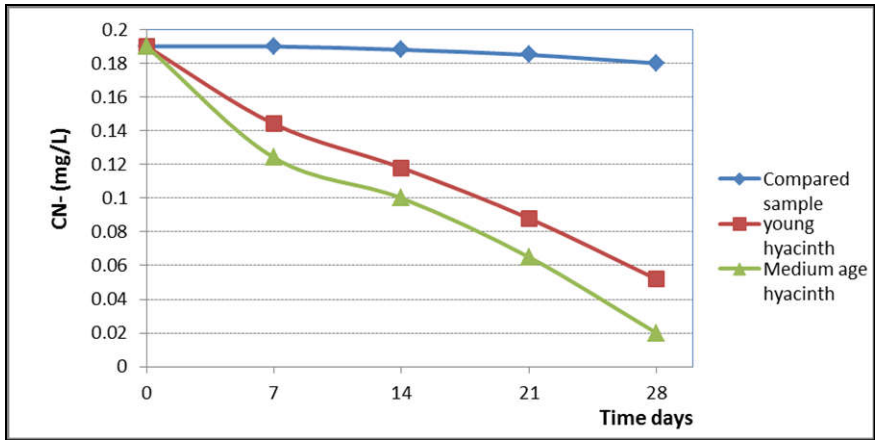


Figure 3.34. The results determining the amount of cyanide in hyacinth samples and control sample feed (control)

From the results on the Table 3.45 and figure 3.34 it shows:

After 21 days treatment, the concentration of cyanide reached criteria B of QCVN 40: 2011/BTNMT limits when discharging industrial effluents into water sources used for drinking water supply. After 28 days treatment, the concentration of cyanide reached criteria B of QCVN 08: 2008/BTNMT limits when discharging industrial effluents into water sources used for drinking water supply. This show that: both young and average age hyacinth are capable of processing handling cyanide, but at average age hyacinth has longer roots, grow stronger and processing capabilities better handle young hyacinth.

CONCLUSION

1.Have examined the optimal conditions and building spectrophotometric calibration curve to determine the amount of cyanide used pyridine – pyrazolone and reagents pyridine - barbutiric. On that basis photometric selection method with reagents pyridine-barbituric reagents to determine the amount of cyanide in the water sample.

- Calibration is built under the optimal conditions: λ_{max} = 580 with molar ratio $n_{Chloramine\ T}$ / n_{CN} = $2.2x10^{-5}$ / $1,9x10^{-7}$ ~ 115; $V_{(TT2)}/V_{CN}$ = 3 / 2.5; time = 30 minutes. Calibration curve equation is as follows

$$A = (2.511 \pm 0.072).C_{CN^-} + (0.018 \pm 0.009)$$

The correlation coefficient R^2 = 0.9985. Linear in the range: 0.01 ÷ 0.30 mg/L

- Limit of Detection: LOD = $3,6.10^{-3}$ (mg / L) = 3.6 ppb
- Limit of quatification: LOQ = 0.012 (mg /L) = 12 ppb

From the results on the board 3.43 shows:

• Recycle 1 (C_{CN^-} = 1.900 mg/L): until to 2nd day appears hyacinth phenomenon dirt poor, weakened trees. From day 3th hyacinth starts wilting and dying. Thus dirt inappropriate in C_{CN^-} = 1.90 mg/L.

• Containers 2 (C_{CN^-} = 0.380 mg/L - diluted 5 times the bucket 1): hyacinth not wither, but grow slowly. After the 7th day phenomenon appears dirt poor hyacinth, weakened hyacinth. From 9th hyacinth starts wilting and death, concentration dropped 0.257 CN mgCN$^-$/L. After 10 days, we stopped feeding hyacinth.

• Containers 3 (C_{CN^-} = 0.190 mg/L - diluted 10 times with box 1): hyacinth grows well, not bad and withered leaves phenomenon. CN concentrations in animal form tapered. By day 14 was 0.104 mg CN/L. Therefore we determined the concentration of CN cease after 14 days. Summary: initial concentration CN huge impact on the growth and development of the hyacinth. We found hyacinth likely grows and develops normally at low cyanide concentration of (C_{CN} = 0.190 mg/L).

3.5.2.3. Results of treatment of plating wastewater samples at Thuy Thanh village, Thanh Oai District, Hanoi

Results of cyanide treatment in waste water in the village of Thanh Thuy plated, Thanh Oai District, Hanoi by hyacinth and control samples (control) not treated with hyacinth are presented in table 3.45 and Figure 3.34.

Table 3.45. The results determining the amount of cyanide in hyacinth samples and control sample feed (control)

Time (days	Compared sample (no hyacinth)		hyacinth			
			Young (box 2)		Medium age (box 3)	
	C_{sampl} (mg/L)	H %	C_{CN} (mg/L)	H (%)	C_{CN} (mg/L)	H (%)
0	0.190	/	0.190	/	0.190	/
7	0.190	0	0.144	24.02	0.124	34.74
14	0.188	1,05	0.118	37.63	0.102	47.37
21	0.185	2,63	0.088	53.64	0.065	65.26
28	0.180	5.26	0.052	72.63	0.020	89.47

CHAPTER 1. OVERVIEW

1.1. CYANIDE AND CYANIDE COMPOUNDS

1.1.2. Origins of cyanide pollution

• Sources of cyanide in wastewater from electroplating facilities

• Sources of cyanide waste from gold mining establishments

1.3. METHOD FOR DETERMINING CYANIDE

1.3.3. Several methods for determining cyanide

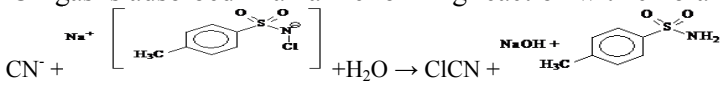
• Determination of total cyanide by spectrophotometric method using chloramine T and pyridine-pyrozalone. This approach was based on the distillation enriched cyanide as HCN gas, then absorbed in an alkaline solution. The content of cyanide (CN^-) was determined by spectrophotometric method using pyridine-barbituric reagent after CN^- was chlorinated by chloramine T created ClCN, then CN^- content was determined by the color compound with pyridine-pyrozalone reagent, using standard curve. Methods for determination of cyanide is conducted in 3 steps:

-Step 1. Distillation, cyanide enrichment. Reactor containing strong acids such as H_2SO_4, here all forms of cyanide complexes including durable form are breaking HCN gas released:

The all types of cyanide + $H_2SO_4 \rightarrow HCN + SO_4^{2-}$ + other products (1.23)

- Step 2. Create compound chlorcianide ClCN

HCL gas is adsorbed in alkaline forming reaction with chloramine-T:



(1.24)

- Step 3. Formation of color compound

Products formed clan reacted with pyridine-pyrazolone reagent to produce blue complex compound using for the determination of cyanide in samples by its absorbance at λ= 614 nm.

• Determination of total cyanide by spectrophotometric method using chloramine -T and pyridine-barbituric

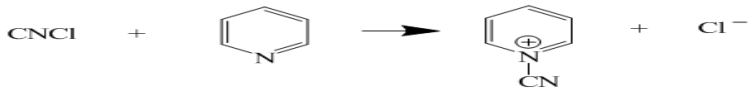
This is a method for determining total cyanide content in water sample. The principle method was conducted similarly to method using pyridine-pyrazolone reagent. Here pyridine-barbituric reagent was used . The obtained color compound is red.

Principle of method: cyanide ion is oxidized by chloramin -T into cyanogen chloride CNCl at pH <8 (to not happen hydrolysis), then chelating with pyridine - barbituric to form red compound having an absorption maxima at 578nm wavelength. These reactions can occur scheduled as follow:

- Chlorination by chloramine T

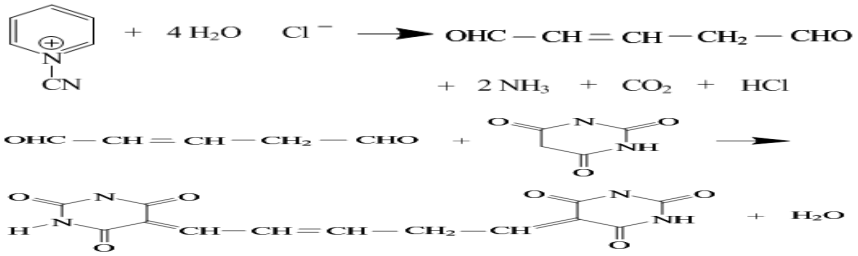
CN + Chloramines-T → ClCN + other products (1.25)

- CNCl reaction with pyridine:



(1.26)

The next reaction is complexing to produce red compound:



Under this method, though some works have, but were found to have the research necessary to obtain accurate analysis results. The study in detail will focused on the selection of equipment, the concentration of chemicals and reagents as well as the reaction time to obtain good experimental results.

1.4. METHODS OF CYANAIDE TREATMENT

1.4.1. Oxidation Method

1.4.2. Electrolysis method

1.4.3. Precipitation method

1.4.4. Biological methods

CHAPTER 2. EXPERIMENTAL PART

2.1. TOOLS, EQUIPMENT, CHEMICALS

2.1.1. Tools, equipment

- The type of flask: 10, 25, 50, 100, 250, 1000 mL and all pipette types.
- The cyanide distillation equipment (KCM) from Behr company (Germany).
- Green filter Paper 390 (Germany), filter diameter of mμ0,45.
- Measuring pH HM - 25R meter produced by TOA Japan. Balance analytical Model GP 150 - 3P, Sartorius Germany, accuracy of ± 0.1 mg.
- Distilled water machine with 2 times of British-made Bibby.
- Spectrophotometer UV-Vis is Libra S60 BIOCHROM British-made.

2.1.2. Chemicals

2.1.2.1. The chemicals used for spectrophotometric method

wastewater, cyanide removal efficiency reached 98.61%. Model M10, wastewater, cyanide removal efficiency reached 99.43%.

3.5.2. Results of cyanide treatment with water hyacinth processing

3.5.2.1. Results determined pH threshold of hyacinth

3.5.2.2. Determination of cyanide threshold of hyacinth

Results determined threshold of 3 barrels of cyanide in each period and the growth of duckweed is presented in Table 3.43:

Table 3.43. Findings CN^- threshold to the growth of hyacinth

Box	Initial conc, ($mgCN^-/L$)	Time t days)	Situation of hyacinth	amount of hyacinth (kg)	Conc,/ t day ($mgCN^-/L$)
1	1.900	0	good	1.00	1.900
		1	bad	/	/
		2	bad	/	/
		3	Wilt	/	/
		5	death	/	/
2	0.380 (f=5)	0	good	1.00	0.380
		1	good	/	/
		2	norm	/	/
		5	norm	/	/
		6	norm	/	/
		7	Bad	/	0.257
		8	Bad	1.05	/
		9	Wilt	/	/
		10	deatht	/	/
3	0.190 (f=10)	0	good	1.00	0.19
		1	good	/	/
		2	good	/	/
		3	good	/	/
		6	good	/	/
		8	good	1.10	0.156
		9	good	/	/
		10	good	/	/
		12	good	1.28	0.124
		13	Nom	/	/
		14	Nom	1.32	0.104

2008.BTNMT (C_{CN} = 0.05 mg/L). Form M1 waste water, cyanide removal efficiency reached 98.66%. Form M2 wastewater, cyanide removal efficiency reached 99.10%. Form M3, efficiency of wastewater treatment reached 99.20% in cyanide. Form M4, efficiency of wastewater, cyanide removal reached 98.89%. Form M5, in wastewater, cyanide removal, efficiency reached 98.93%.

Results of cyanide in wastewater after treatment were taken from the private plating Z in Hai Boi, Dong Anh District, Hanoi are presented in table form in Table 3.42 and Figure 3.33.

Table 3.42. The results of cyanide treatment in wastewater in Z of Hai Boi, Dong Anh, Ha noi

Samples	Cyanide beforev treatment (mg/L)	After treatment (mg/L)	Efficiency (%)
M6	8.05	0.11	98,. 6
M7	7.09	0.06	99.10
M8	7.03	0.06	99.20
M9	7.92	0.09	98.89
M10	7.85	0.08	98.93

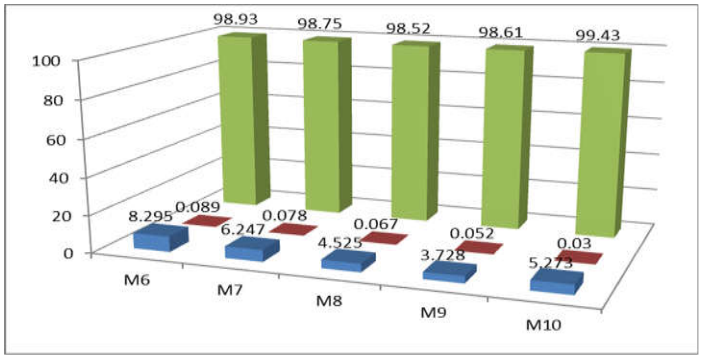


Figure 3.33. The efficiency of cyanide treatment in Z of Hai Boi, Dong Anh, Ha noi

From the results in Figure 3.33 show: sewage outfall in the plating bath of private establishments with very high levels of cyanide, but the trreatment reaction combined with catalyst $Na_2S_2O_5$ and Cu^{2+} give a high cyanide processing performance. Cyanide concentrations after treatment to meet QCVN 40: 2011/BTNMT (C_{CN} = 0.108 mg/L), but the majority has not been reached QCVN 08: 2008.BTNMT (C_{CN} = 0.05 mg/L). Model M6, wastewater, cyanide removal efficiency reached 98.93%. Form M7 wastewater, cyanide removal efficiency reached 98.75%. Form M8, wastewater, cyanide removal efficiency reached 98.52%. Form M9,

1. Phosphate buffer solution ($H_2PO_4^-$ - HPO_4^{2-}), was mixed by a suitable solutions with ther different proportions to obtain a solution with the appropriate pH.

2.Chloramine T, 1% solution: Dissolve 1 gram of chloramine- T ($C_7H_7ClNNaO_2S.3H2O$) in 100 mL of distilled water and kept in cold storage until used. It need, a new challenge every day to be prepared..

3. Pyridine-pyrazolone reagent

- Saturated solution of pyrazole one: Add 0.25 grams of 3-methyl-1-phenyl-2-pyrazolonein-5-one, $C_{10}H_9N_2O$, in 50 ml of distilled water, heated to 60°C and stir, making cool to room temperature. Filter obtain solution (solution a).

- Bispyrazolone solution: dissolve 0.01 g dimethyl-1,1'- 3,3'- diphenyl-[4,4'-bi-2-pyrazolonein] -5,5'-Dione, $C_{20}H_{16}N_4O_2$, in 10 ml pyridine, C_5H_5N, Filter to obtain solution (solution b).

Mix solution solution a with b- solution and stir until the homogeneous filtrate. This heterogeneous reagents (pyridine-pyrazoloneone solution) is pink but not affects the color of the complex, if used within 24 hours from the preparation.

4. Pyridine-barbituric acid reagent.

Weighing 15g $C_4H_3N_2O_3$ barbituric acid, for 250 ml flask, then, adding distilled water (about 100 mL) coated cylinders and then wetting barbituric acid. Add 75 ml of pyridine C_5H_5N and mix. Add 15 ml of concenration HCl followed and shake mix until dissolved barbituric acid and the milky solutiuon turned to yellow and then add 250 mL of distilled water, and mix. This reagent would be stable for about 6 months in cool conditions, in the dark.

5. Original cyanide solution 1000 mg CN /L:

Dissolve 0.1885 g of NaCN and 0.2 g of KOH in distilled water and adjust with the distilled water to in 100 ml flask (or dissolve 2,51g KOH or 2g of KOH in 900ml distilled water).The solution was standardized by 0.0192M $AgNO_3$ solution, with the rhodanine indicator.

6. The standard solutions such as 100; 10; 3; 2; 1 mgCN/L, were prepared from the stock solution 1000 mg CN /L.

8. The solutions $K_4Fe(CN)_6$ with concentrations of 2 and 0.5 $mgCN^-/L$ were prepared.

9. The solution $K_3Fe(CN)_6$ with concentrations of 2 and 0.5 $mgCN^-/L$ were also prepared.

10. NaOH solutions 1.25

11. H_2SO_4 solution, 9M

12. $MgCl_2$ solution: Dissolve 510g $MgCl_2.6H_2O$ in 1000 ml of distilled water.

13. $Na_2S_2O_5$ (sodium metabisulfite solution) 100mg/L, used to prepare solutions with the concentrations of 40 ÷ 70 mg/L;

14. $CuSO_4$ solution concentrations: 15 ÷ 45 mg Cu^{2+}/L.

To determine the amount of cyanide the method can be based on two kinds of the color complexes:

- Blue compound of cyanide with pyridine – pyrazolone reagent.
- Purple rose compound of cyanide with pyridine – barbituric acid reagent.

The survey to choose the good method is necessary. In this thesis, we conducted a survey and construction methods for determining both cyanide with two kinds of reagents mentioned above. From that the evaluation and selection of method with the high sensitivity and better reliability would be established.

2.2. BUILDING METHOD FOR DETERMINING THE CYANIDE WITH PYRIDINE – PYRAZOLONONE REAGENT (T1)

2.3. BUILDING METHOD FOR DETERMINING THE CYANIDE WITH PYRIDINE – PYRAZOLONONE REAGENT (T1)

2.4. DETERMINATION OF THE CONVERSION EFFICIENCY OF STABLE CYANIDE COMPLEX

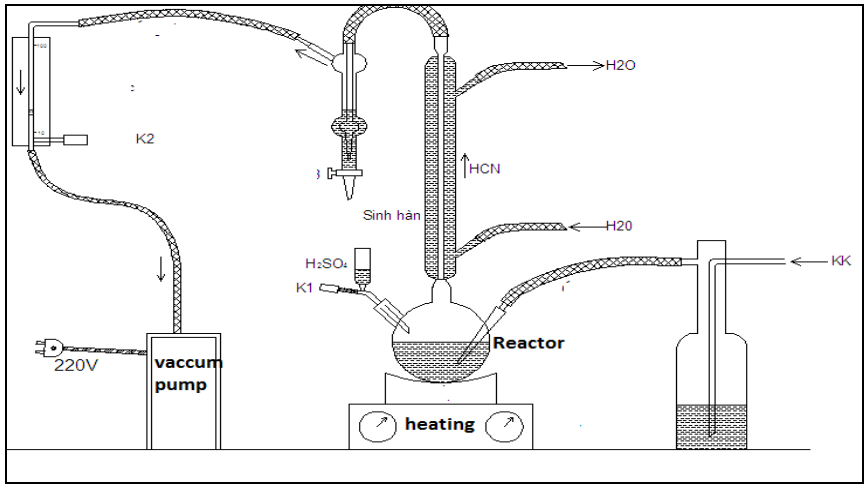


Fig.2.3. Equipment of distillation of cyanide

2.5. DETERMINATION OF THE TOTAL CYANIDE CONCENTRATION IN WASTEWATER

2.5.1. The subject of analysis

- The metal plating enterprises (mainly galvanized) from:

- Companies in Thanh Liet, Thanh Tri District, Hanoi;
- Several plating enterprise in Phuc Tho district, Hanoi;

The wastewater samples in the bath metal plating from Thanh Thuy village, Thanh Oai district and private establishments Z in Hai Boi, Dong Anh District, Ha Noi to be processed by method oxidation with sodium metabisulfite agent and Cu^{2+} using: + $Na_2S_2O_5$ with the concentration of 60mg/L, concentration Cu^{2+} is 30 mg/L.

+ Solution pH is maintained from 9.05 to 9.54 with 0.01 M NaOH

+ The reaction is conducted at room temperature.

Results of cyanide treatment in wastewater were taken from the bath some metal plating places in Thanh Thuy village Thanh Oai District, Ha Noi are presented in table form in Table 3.41 and Figure 3.32.

Table 3.41. The results of cyanide treatment in wastewater in Thanh Thuy, Thanh Oai, Hanoi

Samples	Conc, before treatment (mg/L)	Conc, after treatment (mg/L)	Effciency (%)
M1	8.05	0.11	9866
M2	7.09	0.06	99;10
M3	7.03	0.06	99.20
M4	7.92	0.09	98.89
M5	7.85	0.08	98.93

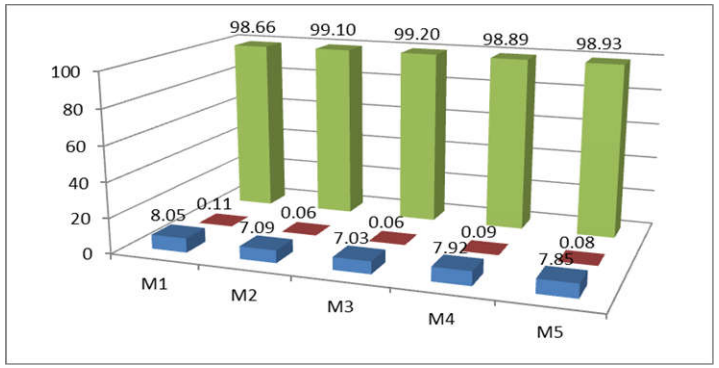


Figure. 3.32. The efficiency of cyanide treatment in wastewater in Thanh Thuy, Thanh Oai, Hanoi

From the results in Figure 3.32 shows that: wastewater at the outfall of the bath of the plating base metal belonging Thanh Thuy village with very high levels of cyanide over react but when treated with combined exposure $Na_2S_2O_5/Cu^{2+}$ environmental effects of the base, the high cyanide processing performance. Cyanide concentrations after treatment to meet QCVN 40: 2011/BTNMT (C_{CN} = 0.108 mg/L) but has not yet reached QCVN 08:

Table 3.32 . The cyanide concentration in Ha Noi

Session	Con. CN^- (mg/L)	Average (mg/L)	Sample exceed QCVN
Dry	0.037 ÷ 4.355	2.196	83/132; 62.9%
Rainy	0.018 ÷ 4,. 92	2.105	55/132; 41,. %
Average	2.150		

3.4.6. The results determine the amount of cyanide in waste water samples at beaches Gold Bank Me, Hop Tien commune, Dong Hy district, Thai Nguyen province

3.4.7. The results determine the amount of cyanide in gold dumps wastewater samples in My Hoa commune Tree Town, Dong Hy district, Thai Nguyen province

3.4.8. General assessment of pollution levels in the region cyanide gold mining in goldfields Bank Me and My Hoa, Dong Cancellation district, Thai Nguyen province

Based on the experimental results we can assess the level of pollution in 02 yards cyanide gold mining Dong Hy district, Thai Nguyen province in both seasons: dry and rainy. Results are presented in Table 3.34.

Table 3.34 . The cyanide concentration in Dong Hy, Thai Nguyen

seasion	Range of Con, CN^- (mg/L)	Average (mg/L)	Samles exceeded QCVN
Dried	0.082 ÷ 1.120	0.601	16/18; 88.9%
Rainy	0.065 ÷ 1.015	0.540	16/18; 88.9%
Average	0.5705		

After sampling and analysis of waste water in the area making gold in gold mines and gold mines Ngan Me, My Hoa village, we found concentrations of cyanide in excess of this are allowed for industrial wastewater and beyond many times to allow for surface water. Especially, wastewater in the neighborhood My Hoa , cyanide content exceeding 10 times than the industrial wastewater (by QCVN 40: 2011/ BTNMT) and exceeded by 27 compared with surface water quality standards, Category B (QCVN 08: 2008/BTNMT). All wastewater contents are discharged directly into the environment without treatment, would seriously affect the health of people of all kinds of livestock as cattle, duck ... then the whole wastewater will go in a small stream flowing over 20km and then flows directly into the Cau river.

3.5. THE TREATMENT OF WASTEWATER FROM METALLIC PLATING CONMANY

3.5.1. Treatment of cyanide by chemical method

3.5.1.1. The factories influencing on the cyanide treatment

3.5.1.2. Results of the practical samples

- Some of the galvanizing facility in Thanh Thuy village, Thanh Oai District, Hanoi;
- Some galvanizing facilities in Dong Anh district, Hanoi.

- The wastewater samples of the gold mining facilities such as:

- Ngan Me, Hop Tien, Dong Hy district, Thai Nguyen province
- My Hoa, Dong Hy district, Thai Nguyen province.
- All water samples are taken according to Vietnam standards (TCVN 5996: 1995).

2.6. RESEARCH ON TREATMENT OF CYANIDE

2.6.1. Handling cyanide by chemical methods

Oxidizing agents are: sodium metabisulfite combining with Cu^{2+} as a catalyst.

2.6.2. Handling cyanide by biological methods

In this thesis, we use the water hyacinth plant to handle cyanide in waste water.

2.6.2.3. Preparation of wastewater samples

Each test session, about 12 liters of electroplating wastewater were collected from the village of Thanh Thuy, Thanh Oai District, Hanoi, diluted 10 times to 120 liters and were divided into sections:

- 2 liters of wastewater were used to determine the initial total concentration of cyanide (after dilution).
- 72 liters of waste water were used for biological treatment, by the water hyacinth plant (adjusted to pH 6.00 pH suitable ÷ 7.00).
- 36 liters of waste water in the tank used for controling (ĐC).

2.6.2.6. Handling cyanide in plating wastewater by water hyacinth plant

Each experimental period consists of 3 boxes in outdoor, with rain cover carefully.

Boxes 1 (DC): wastewater with no hyacinth plant

Boxes 2: wastewater raising 1 kg young hyacinth plant

Boxes 3: wastewater with 1 kg hyacinth plant in medium age

After the period of 7, 14, 21, 28 days sampling determined the concentration of cyanide. When sampling, the distilled water should be added to keep a constant volume for each with 36 liter barrels. For the control sample the cyanide concentration were also be determined for comparison.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. THE CYANIDE DETERMINATION METHOD USING PYRIDINE – PYRAZOLONE (T1)

The optimal conditions of reaction producing color complex compound (between cyanide and reagents pyridine - pyrazolone) are:

- λ_{opt} = 614 nm
- The best pH range = 6.46 ÷ 7.36, selected value: pH_{opt} = 6.95 ± 0.41
- The optimal volume (V) of chloramine T = 0.3 ÷ 0.6 mL, selected V chloramine T/V_{CN-} = 0.3 / 2.5; the molar ratio corresponding to $n_{chloramineT}/n_{CN-} = 1.32.10^{-5}/1.9.10^{-7} \sim 69.5$.
- The range of the optimal reagent volume: V_{T1} = 2.5 ÷ 5.0 ml, V = 3.0 ml or volume ratio: V_{T1} / V_{CN} = 3 /2.5 were chosen for this study.
- Best interval time of color complex compound t = 25 ÷ 50 min; t = 30 minutes was chosen.

3.1.6. Results of the blue cyanide complex absorption spectrogram

The results of 03 absorption spectrograms of blue complex compound in the solution with concentrations C_{CN} = 1; 2; 3 mg/L) are shown in Figure 3.6.

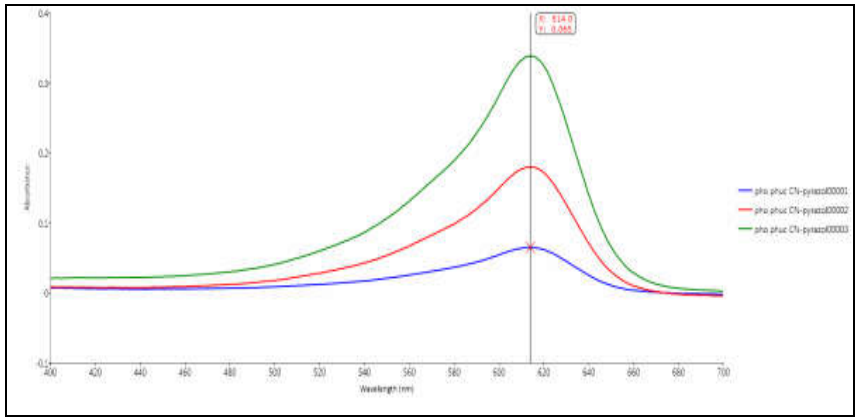
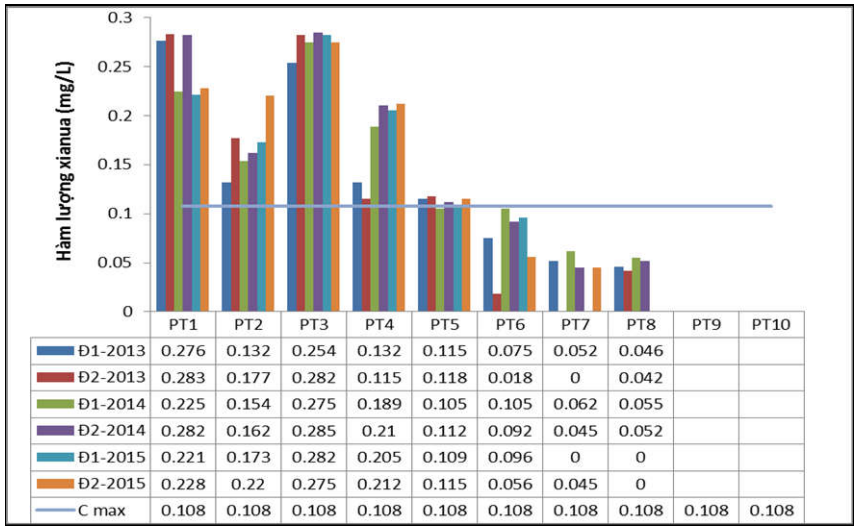


Figure 3.6. The absorption spectrogram of color complexes in the solution with different concentrations

The results on the Figure 3.6 shows:

- The different concentrations of cyanide in solution indicate the different maximum absorbance; the height of the peak is proportional to the concentration of CN;
- Absorption spectrogram of the color complex in solution with the different concentrations of CN^- have the same maximum absorption wavelength λ max = 614 nm in. This proves the color complex



	PT1	PT2	PT3	PT4	PT5	PT6	PT7	PT8	PT9	PT10
Đ1-2013	0.276	0.132	0.254	0.132	0.115	0.075	0.052	0.046		
Đ2-2013	0.283	0.177	0.282	0.115	0.118	0.018	0	0.042		
Đ1-2014	0.225	0.154	0.275	0.189	0.105	0.105	0.062	0.055		
Đ2-2014	0.282	0.162	0.285	0.21	0.112	0.092	0.045	0.052		
Đ1-2015	0.221	0.173	0.282	0.205	0.109	0.096	0	0		
Đ2-2015	0.228	0.22	0.275	0.212	0.115	0.056	0.045	0		
C max	0.108	0.108	0.108	0.108	0.108	0.108	0.108	0.108	0.108	0.108

Figure 3.21. The cyanide concentrations in Phuc Tho, Hanoi

The results seen in Figure 3.21, the cyanide concentrations should be as following:

- The concentration of cyanide in water samples in Phuc Tho in 03 years (2013 ÷ 2015) ranged from 0.042 ÷ 0.283 mg/L. There are 5/10 samples with cyanide content (from 0.109 ÷ 0.283 mg/L) exceed the permitted limit of 1.01 ÷ 2.62 times.
- The average cyanide levels in 03 years were 0.141 mg/L, exceeding 1.30 times the allowable limit.
- The results of analysis of cyanide in 02 seasons (dry season - 1st; rainy season - phase 2) is basically quite similar, but the dry season shallow ditch than be content with a little bit higher cyanide

3.4.3. Results of analysis to determine the amount of cyanide in waste water samples in Thanh Oai District, Ha Noi

3.4.4. Results of analysis to determine the amount of cyanide in waste water samples in Dong Anh district, Hanoi

3.4.5. Overall assessment of cyanide contamination in plating facilities in Hanoi

Based on the experimental results we can assess the concentrations of cyanide in the some districts of Hanoi in both seasons: dry and wet. Results are presented in Table 3.32.

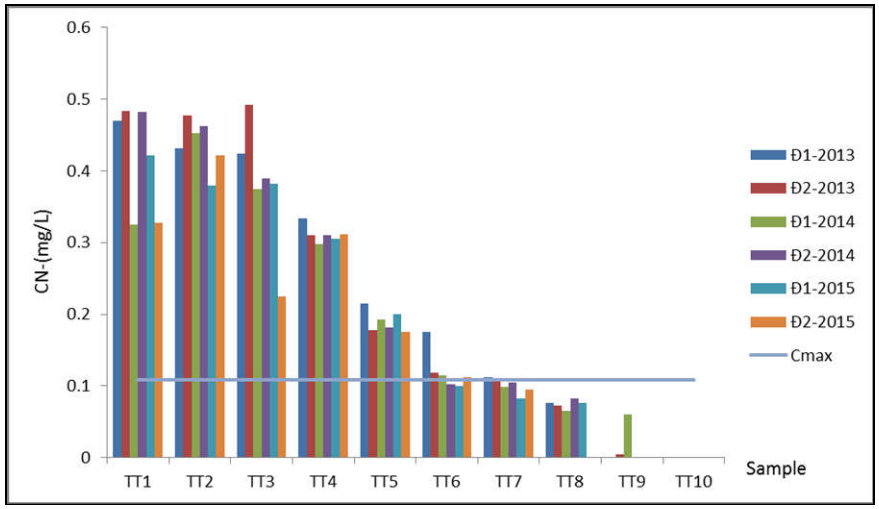


Figure 3.20. The cyanide concentrations in Thanh Tri, Hanoi

Results in Figure 3.19 showed that:

- Concentration of cyanide in water samples in Thanh Tri in 03 years (2013 ÷ 2015) ranged from 0.005 ÷ 0.492 mg/L.
- There are 7/10 of samples having cyanide content (from 0.110 ÷ 0.492 mg/L) exceed the permitted limit of 1.08 ÷ 4.92 times.
- The average cyanide concentrations in 03 years were 0.249 mg/L, exceeding 2.30 times the allowable limit.
- Concentration of cyanide in the samples tended to decrease gradually from sample TT1 (upstream) to the TT10 (downstream). Especially in 02samples, TT9 and TT10 samples, were undetectable cyanide. So thus, the sample, the more resources are diluted by the resources, more and more and lower levels of cyanide.
- The results of analysis of cyanide in 02 seasons (dry season - 1st; rainy season - phase 2)were basically quite similar, but in the dry season shallowed the cyanide content with a little bit higher .

3.4.2. Results of analysis of the amount of cyanide in wastewater samples of Phuc Tho district, Hanoi

3.4.2.4. Overall assessment cyanide contamination in waste water of company in the United plating, Phuc Tho, Hanoi

To assess the overall pollution levels of cyanide in waste water of plating company Phuc Tho, Hanoi in 03 years (2013 ÷ 2015), we denote the results of analytical data in Figure 3.21

compound is stable and has the same composition with the reagent of pyridine. It is empirically optimized wavelength, used for further measurements. This is consistent with the documents . So we choose: $\lambda_{opt} = \lambda max = 614$ nm.

3.1.8. The standards curve to determine the amount of cyanide using pyridine - pyrazolone (T1) reagent

The standard curve for determining cyanide presented in Figure 3.8a.

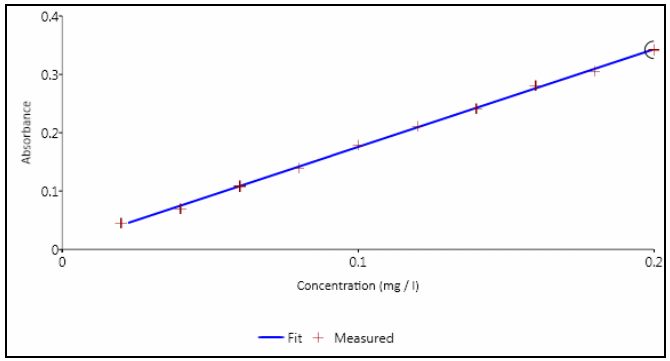


Figure 3.8a. The standard curve determining cyanide with pyridine-pyrazolone

The Curve in Figure 3.8a corresponds to the optimum conditions (pH= 6.95 ± 0.41, reaction time = 30 minutes, $\lambda max = 614$ nm);

To facilitate the measurement and calculation of absorbance (A) and concetration of CN, we baseline statistical treatment under Orgin 8.0 software. Results are presented in Figure 3.8b.

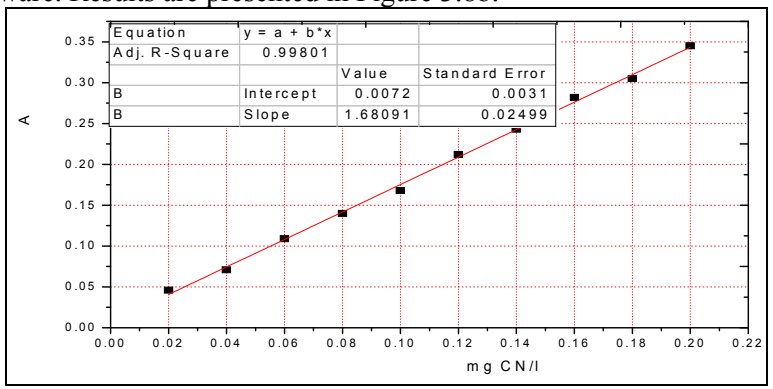


Figure 3.8b. The standard curve determining cyanide using pyridine-pyrazolone (using Orgin 8.0 software)

The calibration equation in this case is

$$Abs = (1{,}681 \pm 0{,}056).C_{CN} + (0{,}007_2 \pm 0{,}006_9) \qquad (PT.1)$$

This equation is satisfied with the correlation $0{,}99 \le R^2 \le 1$.

3.1.9. The results using calibration equation in determination of cyanide using pyridine-pyrazolone (T1)

Results of measuring the absorbance (A) of color complex of cyanide in 10 solutions was conducted in parallel with the same cyanide concentration of 0.02 mg/ L and the calculated cyanide concentrations (based on calibration equation) are presented in Table 3.8.

Table 3.8. Result of absorbance (A) and the calculated cyanide concentration C_{CN}

Sol.	$V_{CN-\ 2\ mg/L}$ (mL)	Additive solutions (mL)	V total (mL)	A	C_{CN^-} (mg/L)
base	0.0	- 0.3 mL chloramine T, mix for 3 min - 2.5 mL solution $H_2PO_4^-$ and 2.5mL solution HPO_4^{2-} - 3 mL pyridin – pyrazolon reagent	50	0.00	0.000
1	0.5		50	0.047	0.025
2	0.5		50	0.039	0.020
3	0.5		50	0.046	0.024
4	0.5		50	0.046	0.024
5	0.5		50	0.044	0.023
6	0.5		50	0.041	0.021
7	0.5		50	0.044	0.023
8	0.5		50	0.048	0.025
9	0.5		50	0,046	0.024
10	0.5		50	0.047	0.025

The standard deviation $SD = \sqrt{\frac{\sum (A_i - \overline{A})^2}{n-1}} = 0.0017$

Average concentration value: $\overline{C} = 0.023$

Limit of detection : LOD = 3.SD = 3x 0.0017 = $5.1.10^{-3}$ (mg/L) = 5.1 ppb

Limit of quantification: LOQ = 10xSD = 10x0.0017 = 0.017 (mg/L) = 17 ppb

Control $R = \frac{\overline{C}}{LOD} = \frac{0{,}023}{5{,}1.10^{-3}} = 4{,}51$

R is satisfied with 4 < R < 10, the tested concentration of C_{CN} = 0.02 mgL is accepted and obtained LOD is satisfied.

- Determination of recovery (to determine the right)

wastewater samples of plating companies at Thanh Liet, Thanh Tri, Hanoi 2015 are presented in Table 3.31.

Table 3.31. The CN^- concentration in wastewater in plating companies Thanh Liet, Thanh Tri, Hannoi 2015

Location	Periodа 1-2015			Periodа 2 -2015		
	pH	C_{CNtb} (mg/L)	C_{Aveg}(mg/L)	pH	$C_{CNtAver}$ (mg/L)	C_{Aver}(mg/L)
TT1	8.15	0.421	0.421±0.001	8.20	0.328	0.328±0.004
TT2	8.22	0.379	0.379±0.001	8.18	0.422	0.422±0.006
TT3	8.27	0.382	0.392±0.003	8.25	0.225	0.225±0.004
TT4	8.25	0.305	0.305±0.003	8.22	0.312	0.312±0.004
TT5	8.25	0.200	0.200±0.006	8.18	0.175	0.175±0,. 05
TT6	8.47	0.100	0.100±0.003	8.28	0.112	0.112±0.004
TT7	8.15	0.083	0.083±0.004	8.20	0.095	0.095±0.006
TT8	7.68	0.076	0.076±0.003	7.75	no detec.	no detec
TT9	7.92	no detec.	no detec.	8.00	no detec.	no detec.
TT10	8.10	no detec.	no detec.	8.05	no detec.	no detec.

From the results on the Table 3.31 it shows:

- Concentration of cyanide in wastewater samples of the plating company in Thanh Tri, 2015 ranged from 0.076 ÷ 0.422 mg/L. There 6/10 sampling location, cyanide content exceeds permissible limits, accounting for 60%.
- Analytical results in two tranches in 2015 in 10 locations also showed that the average content was 0.243 mg/L in the peroda 1; The average concentration was 0.209 mg/L in the peroda 2; Average year was 0.226 mg/L.
- The cyanide analytical results of 2015, lower than in 2013 and 2014.

3.4.1.4. Overall assessment of cyanide contamination in waste water of plating company in Thanh Liet, Thanh Tri, Hanoi

To assess the overall pollution levels of cyanide in waste of water plating companies Thanh Liet, Thanh Tri District, Hanoi in 03 years (2013 ÷ 2015), we denote the analytical results in Figure 3.20.

The results in Table 3.26 shows:

- For the solution of $[Fe(CN)_6]^{4-}$ the concentrations redefine approximate initial concentration.
- For the solution of $[Fe(CN)_6]^{3-}$ the concentrations redefined by 0.021 mg/L (only 84%), this may be due to the complex $[Fe(CN)_6]^{3-}$ stable constant $\beta_6 = 10^{43,9}$ > stable constants of the complex $[Fe(CN)_6]^{4-}$ ($\beta_6\ 10^{31,9}$)

3.3.3. The recovery of the cyanide in solution

Table 3.27. The recovery of $[Fe(CN)_6]^{4-}$

	Sample + 0.01mg CN^-/L	R%	Sample+ 0.02mg CN^-/l	R%	Sample+ 0.04mgCN^-/l	R%
1	0.033	110	0.040	90	0.066	110
2	0.038	110	0.046	95	0.063	90
3	0.034	100	0.046	110	0.061	92.5
4	0.037	90	0.050	110	0.061	82.5
5	0.035	90	0.048	110	0.064	95
6	0.033	80	0.042	85	0.068	107.5
R_{TB}%		**96.7**		**100**		**96.3**

The results determining the recovery of complex solution $[Fe(CN)_6]^{3-}$ is presented in Table 3.28

Table 3.28. The recovery of complex solution $[Fe(CN)_6]^{3-}$

	Sample + 0,01mgCN^-/L	R%	Sample + 0,02mg CN^-/L	R%	Sample + 0,04mgCN^-/L	R%
1	0.030	90	0.037	80	0.063	105
2	0.028	90	0.040	105	0.060	102.5
3	0.029	90	0.041	105	0.059	97.5
4	0.033	80	0.042	85	0.061	90
	0.025	80	0.039	110	0.056	97.5
6	0.032	110	0.042	105	0.055	85
R_{TB}%		**90**		**98.3**		**96.3**

The results in Table 3.27 and 3.28 shows: the average recovery ranges from 90 ÷ 100%, totally guaranteed as prescribed by AOAC (allowing 110% ÷ 80) [23]. That confirms the withdrawal of the complex containing cyanide solution is reliable, that means in the stable complexes ion CN^- after distillation was liberated almost entirely in the form of HCN gas.

3.4. DETERMINATION OF TOTAL CYANIDE IN WASTEWATER

3.4.1. Determination of total cyanide in wastewater from Thanh Tri, Hanoi

3.4.1.3. The total cyanide concentrations 2015

The results of analysis to determine the amount of cyanide in

Table 3.10. Results determining the cyanide recovery of method using pyridine - pyrazolone reagent.

Sample		Blank sample C_{CN} = 0.02 mg/L		Blank sample + standard sol. C_{CN} = 0.1 mg/l		Blank sample + standard sol. C_{CN} = 0.2 mg/l	
	Nr measuring	Results (mg/L)	R%	Result (mg/L)	R%	Result (mg/L)	R%
Con, C_{tt} (mg/L)	1	0.016	80	0.096	96	0.176	88
	2	0.022	110	0.094	94	0,193	96.5
	3	0.020	100	0.108	108	0.191	95.5
	4	0.018	90	0. 02	102	0.140	70
	5	0. 19	95	0.104	104	0.188	94
	6	0.014	70	0.089	89	0.185	92.5
Average recovery			90.8		98.8		89.4

• Results in Table 3.10 (in CT.7) showed: The average recovery ranged from 89.4 ÷ 98.8% guaranteed (by AOAC allowed from 80 ÷ 110%). That confirms the guarantees of withdrawal, or the correct warrant.

3.1.9.3. Determination of method repeatability (repeatability).

Table 3.11. Optical density and concentration calculations of the color complex solution with different cyanide concentrations (low, medium, high)

Real conc (mg/l)		**0.02**	**0.10**	**0.20**
Calc. conc. (mg/L)	Time 1	0.016	0.096	0.176
	Time 2	0.022	0.094	0.193
	Time 3	0.020	0.108	0.191
	Time 4	0.018	0.102	0.140
	Time 5	0.019	0.104	0.188
	Time 6	0.014	0.089	0.185
	Average	0.018	0.0999	0.178
SD		0.0028	0.0070	0.0198
RSD (%)		15.71	7.03	11.09
RSD (%) under AOAC		15-21	<15	11 -15

Results on table 3.11 showed that the relative standard deviations were compared with AOAC guarantee. That assertion ensures repeatability, and ensures precision.

Accuracy = trueness (measured returns to deviate Bias) + precision (repeatability)

Thus the method used to determine the amount of cyanide by spectrophotometric method using the reagent pyridine - pyrazolone ensures the accurate, reliable.

3.2. METHOD DETERMINATION OF CYANIDE WITH PYRIDINE- BARBITURIC REAGENT (T2)

3.2.6. Results of purple pink complex absorption spectrometry

Results of 03- complex absorption spectrograms in solution with the concentration C_{CN-} = 1; 2; 3 mg / L) are shown in Figure 3.14.

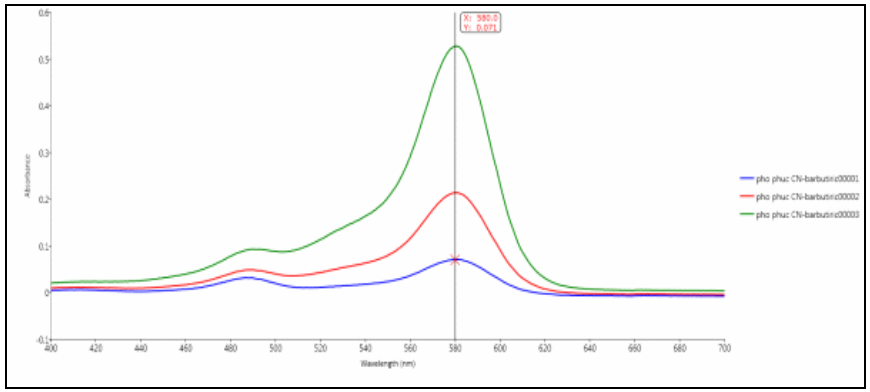


Figure 3.14. Absorbance spectrogram of color complex compounds with pyridine – barbituric reagent

The results on the Figure 3.14 shows:

- The different concentrations of cyanide in solution indicate the different maximum absorbance; the height of the peak is proportional to the concentration of CN;
- Absorption spectrogram of the color complex in solution with the different concentrations of CN^- have the same maximum absorption wavelength λ max = 580 nm in. This proves the color complex compound is stable and has the same composition with the reagent of pyridine. It is empirically optimized wavelength, used for further measurements. From here, the optimal experimental wavelength would be found used for subsequent measurements. So we choose: λmax = 580 nm.

3.2.10. Evaluatation of two methods of determining the concentration of cyanide and select the appropriate method for determining cyanide in the practical samples

Table 3.23. Matrix of parameters of the two methods to determine CN^-

	Method with pyridine – pyrazolone	Method with pyridine – barbituric
Optimal conditons	- λ_{max} = 614nm - pH_{opt} = 6.91 ± 0.45 - $n_{CloraminT}/n_{CN} = 1.32x10^{-5}/1.9x10^{-7} \sim 69,5$. - V_{T1}/V_{CN} = 3.0/2.5 - t_{opt} = 15 ÷ 40 min	- λ_{max} = 580nm - pH_{opt} = 6.13 ± 0.29 - $n_{Cloramin\ T}/n_{CN} = 2.2x10^{-5}/1.9x10^{-7} \sim 115$ - V_{T2}/V_{CN} = 2.5/2.5 - t_{opt} = 15 ÷ 50min
calibra. pltot	Equat. Abs = (1.681 ± 0.056).C_{CN} + (0.007_2 ± 0.006_9)	- Equat. Abs = (2.511 ± 0.072).C_{CN} + (0.018 ± 0.009)
Range of application	Prop.. range 0.01 ÷ 0.30 mg/L - LOD = $5.1x10^{-3}$ mg/L = 5.1 ppb - LOQ = 0.017 mg/L = 17 ppb	Prop.. range 0.01 ÷ 0.30 mg/Lg/l - LOD = $3.60x10^{-3}$ mg/L= 3.6 ppb - LOQ = 0.012 mg/L= 12 ppb

3.3. Determination of conversion capacity of stable complex of cyanide

3.3.2. The results determine the concentration CN^- in the complex after distillation

Table 3.26. Determination of CN^- in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ after distillation

Samples	v^o_{DDX} (mL)	C^o_{CN} theoretica 50mL (mg/L)	C_{CN} (mg/L)	Average C_{CN-} (mg/L)	H (%)
$[Fe(CN)_6]^{4-}$ (0.5mg/L)	2.50	0.025	0.022	0.025 ± 0.002	100 ± 0.08
			0.027		
			0,024		
			0.028		
			0.0 25		
			0.026		
			0.023		
$[Fe(CN)_6]^{3-}$ (0.5mg/L)	2.50	0.025	0.021	0.021 ± 0.001	84 ± 0.02
			0.019		
			0.020		
			0.250		
			0.017		
			0.021		
			0.022		