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A study of Accuracy of Multicomponent analysis of Phenol and cyanide in their binary Solution by Colorimetric Method

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Abstract

The present work delineates the accuracy of colorimetric method for the determination of phenol and cyanide in their binary solution. The effect of phenol on cyanide estimation and vice versa has been studied by estimating a known concentration of each pollutant in solutions with different concentration ratios of both phenol and cyanide. Aliquots prepared with constant concentration of one component and varying concentration of the other component were analyzed for the impact studies of both the components on each other. Error calculations were also carried out for estimation of both components in their individual solutions as well as in their binary solutions. Studies of bond formations between components and components with their coloring agents were carried out. The study of effect of coloring agents on the absorbance and corresponding wavelengths were also carried out.

Keywords: Colorimetric, phenol, cyanide, aliquots, pollutants, absorbance.

Introduction

Water pollution, one of the forever challenges for the environmentalist has always been posing a problem for a healthy life survival. The sources of water pollution include domestic, industrial, agricultural waste etc.[1,2]. Removal of the harmful water pollutants has always been a priority for the environmentalist. A major source of industrial waste water includes the coke waste waters which constitute of phenols and cyanides[3] which are quite hazardous for human existence. Prior to the discharge of the waste water contaminated with phenol and cyanide it is mandatory to be treated to reduce the concentration as per the standards. The MCL (Maximum Contaminant Level) of phenol and cyanide in industrial discharge is set to be 0.5 mg/L and 0.2 mg/L[3]. The prerequisite to the treatment of contaminated waste water is the determination of the amount of pollutant to be removed. The method used for the analysis should be accurate, economic, less time consuming and not very tedious. It should be able to estimate the pollutant concentration accurately and without requiring a lot of efforts.

In the present work the authors have focussed on determining whether colorimetric method can be used accurately for phenol and cyanide estimation in their binary solution. The impact of both phenol and cyanide on each other as well as on their analysis procedure using colouring agents is studied.

Literature Review: There are many methods for the estimation of phenol which include High pressure liquid chromatography (HPLC)[4], high pressure liquid chromatography/ mass spectrometry (HPLC/MS)[5], high-resolution gas chromatography with negative chemical ionization mass spectrometric detection (HRGC-(NCI)-MS)[6], colorimetric method[7,8] gas and liquid chromatography (GC), liquid chromatography. Similarly the methods used for cyanide estimation include High pressure liquid chromatography (HPLC)[9], electrophoresis[10], acid hydrolysis method[11], ion chromatography[12], phenolphthalein method[13], colorimetric method[3,14].

In the recent works[3,15] simultaneous removals of phenol and cyanide from a binary mixture is considered instead of their individual removal from waste water. For this process generally colorimetric method is used for the estimation of phenol and cyanide. The methods used for phenol and cyanide analysis were the colorimetric method using 4-aminoantipyrine and picric acid[3] respectively using a uv-vis spectrophotometer.

Reagents: All the chemicals used in this study were of analytical grade and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. 0.189 g of NaCN was dissolved in 1L of millipore water (Q-H_2O, Millipore Corp. with resistivity of 18.2 MX-cm) to prepare a stock solution of cyanide concentration of 100 mg/L. The pH of the cyanide stock solution was adjusted to 10 using 1 N NaOH. The phenol stock solution, with the concentration of 1000 mg/L, was prepared by adding 1 g of pure phenol crystals to 1 L of millipore water. Finally a binary mixture stock solution of 1000 mg/L phenol and 100 mg/L cyanide was prepared by the individual stock solutions.

Coloring agents for phenol analysis: 2g Aminoantipyrine was dissolved in 100 mL millipore water to make 20 g/L 4-Aminoanitipyrine solution. Solution of 80 g/L potassium ferricyanide solution ($K_3Fe(CN)_6$ was prepared by adding 8g in 100 mL millipore water. Buffer solution was prepared by adding Ammonium Hydroxide (NH_4OH) and Ammonium Chloride (NH_4Cl).

Coloring agents for cyanide analysis: 1 L of buffered picric acid solution was prepared by dissolving 40 g of DTPA (Diethylenetriamine), 16 g of Sodium hydroxide in 900 mL millipore water then 6 g picric acid, 14 g of anhydrous sodium tetraborate and 8 g Sodium carbonate. 100 mg/L Nickel solution was prepared by disolving 0.22 g of $NiSO_4$ and 1 g of NaCl in 500 mL millipore water (Picric acid method).

Methodology

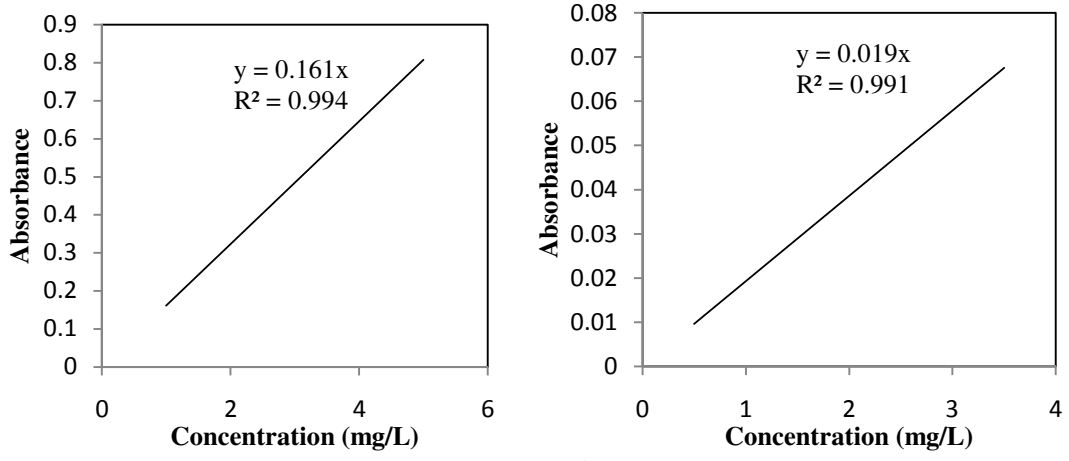
Calibration curves were drawn for both phenol and cyanide in the concentration range of 1 mg/L to 5 mg/L. 10 mg/L phenol solution was prepared from the phenol stock solution of 1000 mg/L. Similarly 10 mg/L cyanide solution was prepared from cyanide stock solution of 100 mg/L. Then different binary solutions were prepared containing 10 mg/L phenol and 10 mg/L cyanide i.e. in the ratio of 1:1 for phenol and cyanide, 10 mg/L phenol and 20 mg/L cyanide i.e. in the concentration ratio of 1:2, 10 mg/L phenol and 40 mg/L cyanide for 1:4 concentration ratio, 1:5 concentration ratio by 10 mg/L phenol and 50 mg/L cyanide and finally 1:10 ratio by 10 mg/L phenol and 100 mg/L cyanide. Similarly solutions were prepared containing constant cyanide concentration and varying phenol concentration. For the analysis of binary mixture containing phenol and cyanide, these solutions were first divided into two parts and then one part was subjected to the colorimetric method of phenol analysis to estimate phenol concentration and the other part was subjected to cyanide analysis to estimate cyanide concentration. To evaluate the impact of one component over the analysis of other component the absorbance was measured at different concentration ratios of both the components.

The individual solutions of 10 mg/L of phenol and cyanide were first analysed without using coloring agent by a UV-VIS spectrophotometer and then they were analyzed using colorimetric method. The aliquots containing constant phenol and varying cyanide concentrations were then analyzed for phenol using 4-aminoantipyrene, potassium ferricyanide and buffer solution at a wavelength of 510 nm. Similarly the aliquots containing constant cyanide and varying phenol concentrations were analyzed using picric acid reagent and nickel solution at a wavelength of 520 nm. Absorption spectra were also prepared for both phenol and cyanide using a UV-VIS spectrophotometer in the wavelength range of 190 nm to 700 nm.

Results and Discussion

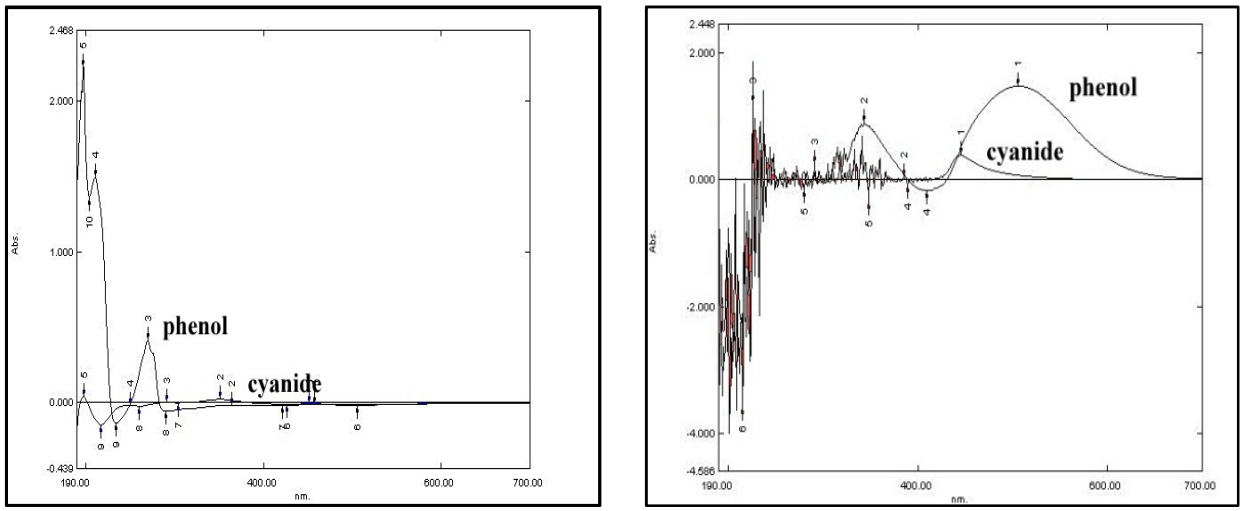
Figure-1 (a) shows the calibration curve of phenol by colorimetric method and figure-1 (b) shows the calibration curve of cyanide by colorimetric method.

Figure-2 (a) shows the absorption spectra of both phenol and cyanide in their individual solutions with water as a solvent in the wavelength range of 190nm to 700 nm. Figure-2 (b) shows the absorption spectra of both phenol and cyanide with their respective coloring agents taken with the help of a uv-vis spectrophotometer in the range of 190 nm to 700 nm. From Figure-2 (a) it can be seen that there is a slight overlapping of spectra of phenol and cyanide but with their colouring agents i.e. from Figure-2 (b) it is clearly visible that the individual absorption spectrum of phenol and cyanide does not overlap each other especially in the wavelength range of 400 nm to 600 nm which is the actual range for colorimetric analysis. According to table-1 phenol shows a peak absorbance of 1.614 at a wavelength of about 506 nm and cyanide shows a maximum peak of 0.189 at 445 nm.



(a) (b)

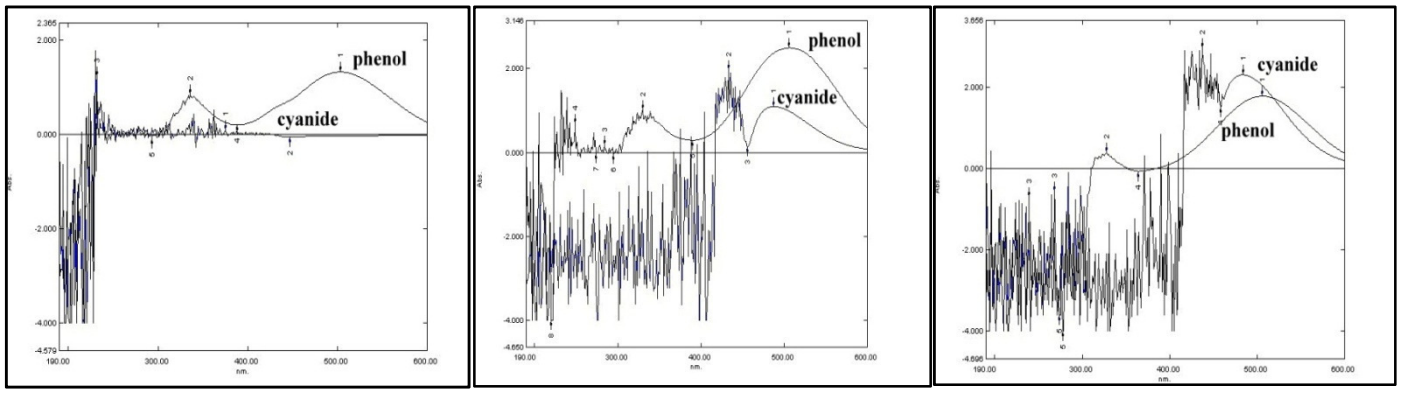
Figure-1
(a) Calibration curve for phenol (b) Calibration curve for cyanide, by colorimetric method at a wavelength of 510 nm and 520 nm respectively



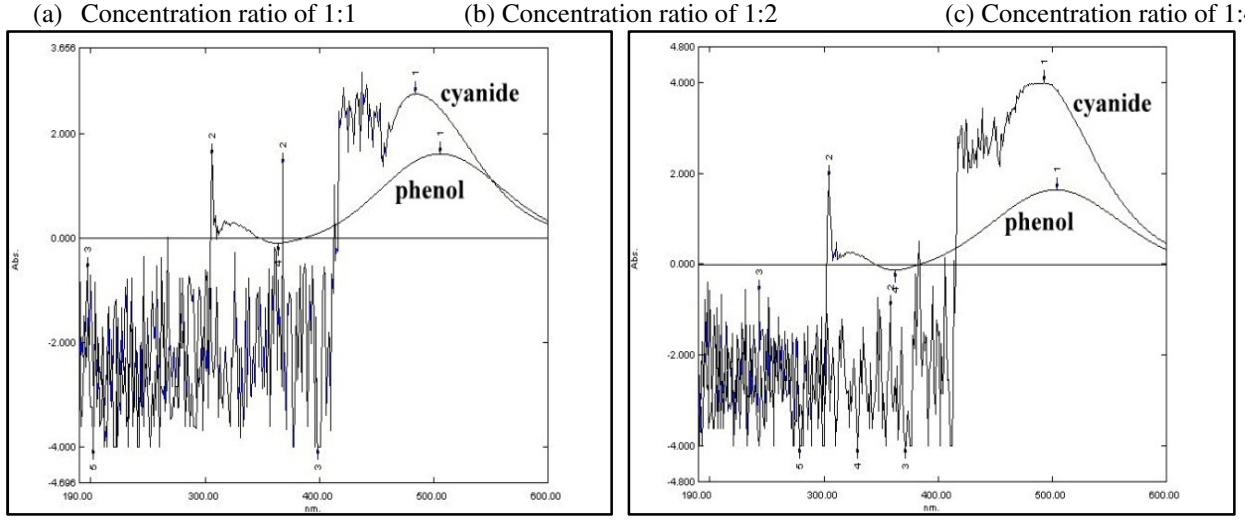
(a) (b)

Figure-2

(a) Absorption spectra of phenol and cyanide without colouring agents in their individual solutions (b) Absorption spectra of phenol and cyanide in their respective solutions with colouring agents



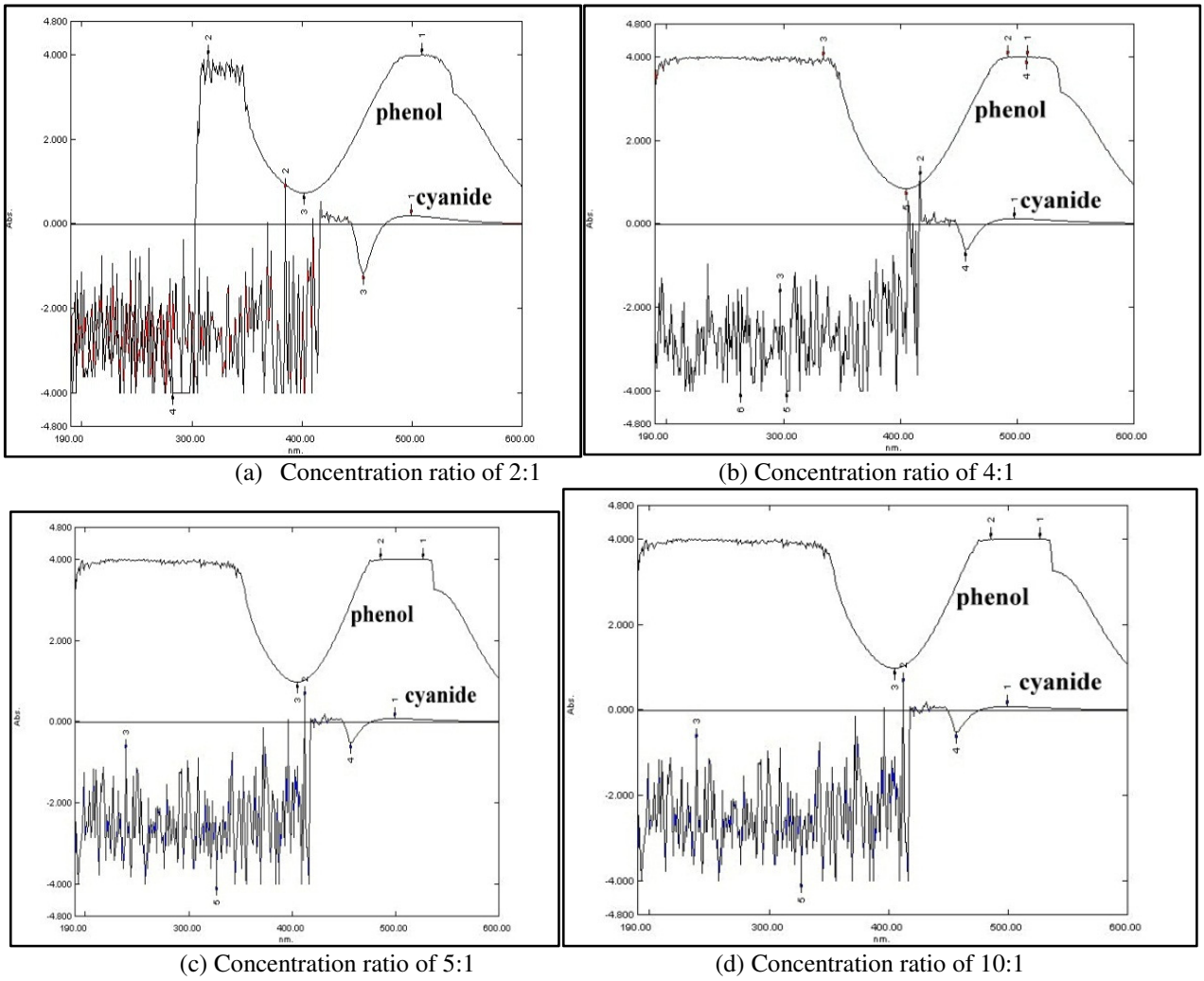
(a) Concentration ratio of 1:1 (b) Concentration ratio of 1:2 (c) Concentration ratio of 1:4



(d) Concentration ratio of 1:5 (e) Concentration ratio of 1:10

Figure-3

Absorption spectra of phenol and cyanide in constant phenol and variable cyanide concentrations



(a) Concentration ratio of 2:1 (b) Concentration ratio of 4:1

(c) Concentration ratio of 5:1 (d) Concentration ratio of 10:1

Figure-4
Absorption spectra of variable phenol and constant cyanide concentration

Table-1
Phenol and cyanide peak absorbances and their corresponding wavelength

Phenol Concentration (mg/L)	Cyanide Concentration (mg/L)	Peak absorbance for phenol	Peak absorbance for cyanide	Wavelength (phenol) nm	Wavelength (cyanide) nm
10	-	1.614	-	506	-
-	10	-	0.193	-	445
10	10	1.457	0.189	503	375
10	20	2.212	1.096	506	487
10	40	1.698	2.312	506	484
10	50	1.619	2.769	506	484
10	100	1.643	4	504	493
20	10	4	0.191	509	499
40	10	4	0.178	509	498
50	10	4	0.165	527	499
100	10	4	0.199	467	494

Table-2
Phenol and cyanide concentrations as obatined by their absorbance using regression equation along with percentage error in phenol and cyanide determination

Concentration Ratio Phenol: Cyanide	Phenol Conc. (mg/L)	Cyanide Conc. (mg/L)	Phenol Conc. From absorbance	Cyanide conc. From absorbance	Phenol % Error ± % Error	Cyanide % Error ± % Error
1:1	10	10	9.027	9.79	9.73	2.1
1:2	10	20	13.70	-	37	-
1:4	10	40	10.52	-	5.2	-
1:5	10	50	10.03	-	0.3	-
1:10	10	100	10.17	-	1.7	-
2:1	20	10	-	9.89	-	1.1
4:1	40	10	-	9.22	-	7.7
5:1	50	10	-	8.54	-	14.6
10:1	100	10	-	10.31	-	3.1

Table-1 further depicts the peak absorbances of both phenol and cyanide in their binary solutions of different concentration ratios along with their corresponding wavelength. Table-2 depicts the concentration of phenol and cyanide as calculated by the absorbance with the help of regression equations obtained by the calibration curves. This table also depicts the percentage error attained in all the cases. For the concentration ratio of 1:1 both the phenol and cyanide concentrations obtained from their absorbance in their binary solutions are quite comparable to their known concentrations in the aliquots.

For phenol and cyanide concentration ratio of 1:2 there is a noticeable error in the phenol concentration obtained by the absorbance which can be attributed to human error as phenol concentrations for the rest of the aliquots with concentration ratio of 1:4, 1:5 and 1:10 are quite comparable to its known concentration. Also the wavelegth corresponding to the peak phenol absorbance also lie in the range of 503 nm to 506 nm which is quite close to the phenol analysis wavelength of 510 nm. For cyanide all the aliquots containing constant cyanide and variable phenol concentration almost show the same absorbance showing a less error percentage in cyanide determination in the binary solution of phenol and cyanide. However for the phenol and cyanide concentration ratio of 5:1 there is a noticeable error percentage but this can also be a case of human error.

Further proving the non-interfering nature of phenol and cyanide in their analysis procedure are the absorption spectra achieved for their binary solutions of different concentration ratios. Figure-3 and figure-4 show the absorption spectra of phenol and cyanide in their binary solutions of different concentration ratios. The unchanged absorbance of the aliquots for the individual component analysis in the presence of increasing concentration of the other component in the binary mixture adheres to the fact of non-overlapping absorption spectrum of individual components[16]. Analyzing figure-3 and figure-4 also brings forth that there is a slight difference in peak absorbance achieved at their respective peak wavelengths which may be attributed to the trace impurities present in the solution and also to the certain time lapse in evaluating solutions of different concentrations or simply a result of human error. The non-overlapping spectra of these compounds and a comparatively less difference in absorbance proves that zero-order UV spectroscopy can be used for quantification of both the compounds when present simultaneously and regression analysis is not a requisite to further validate it[16].

Since the concentration is directly proportional to the absorbance which proves that the solution follows Beer-Lambert Law which in turn proves that there is no complex formation between solute and solvent. This also validates that there is no complex formation between phenol and cyanide or between cyanide and phenol and their respective coloring agents[17]. As evident from figure-2 (b), figure-3 and figure-4 there is not much difference between the structures of absorption band of both the components when present in their individual solution and when present in their binary mixtures when recorded in the presence of their respective coloring agents which shows that cyanide does not hydrogen bond with phenol in their binary mixture[17]. The solvent consisting of coloring agents stabilizes the solutions of both phenol and cyanide i.e. decreases the energy required to produce a transition from an occupied electronic level to an unoccupied energy level which is very evident from the fact that the wavelength corresponding to peak absorbance increases in the presence of solvents.

These results for phenol and cyanide analysis in their binary mixtures at different concentration ratio show that different concentration ratios of binary mixture and increasing cyanide concentration does not have an impact on phenol determination by colorimetric method. Similarly the aliquots containing different phenol concentrations also show that the increasing phenol concentration has no impact on cyanide analysis by colorimetric method.

Conclusion

Simultaneous co-adsorption of phenol and cyanide from a wastewater sample requires the accuracy of analysis of phenol and cyanide in their binary mixture. The samples of different concentrations of phenol and cyanide were individually analyzed for both the components and their absorption spectra were also taken at different concentration using a uv-spectrophotometer. The absorption spectra appeared to be non-overlapping and the absorbance of individual components appeared to be almost same at binary mixtures of different concentrations. Hence the study reveals that phenol and cyanide can be easily analyzed in their binary solutions by zero order UV spectroscopy with a high level of accuracy. Further study also revealed that cyanide does not form a hydrogen bond with phenol or with the coloring agents of phenol and vice versa. A bathochromic shift has also been observed in the analysis using coloring agents i.e. the coloring agents decrease the transition energy from one energy level to another thereby increasing the wavelength.

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