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Determination of 1,4-dichlorobenzene in Industrial waste water

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ABSTRACT: A new, simple and selective spectrophotometric method has been developed for the determination of trace amount of 1,4 dicholorobenzene (p-dichlorobenzene or PDCB) . This method is based on the formation of golden yellow coloured mixed complex of PDCB with N-PBHA (N-Phenyl benzo hydroxamic acid). The molar absorptivity of PDCB – NPBHA complex in chloroform at the absorption maxima of 443nm was calculated to be $9.355X10^5$ litre mol^{-1} cm^{-1}. The system obeyed Beer's law between0.0121 – 0.0512. Most of the foreign ions do not interfere in the proposed method. The method has been successfully applied for the determination of trace analysis of PDCB in industrial waste water with Relative standard deviation was found to be1.44%.

Keywords: Chloroform, reproducible, sensitive, N-Phenyl-benzo-hydroxamic acid and PDCB

I. INTRODUCTION

Many trace pollutants are emitted by the combustion processes taking place in motorized vehicles or industrial incinerators, one of which is 1,4-dichlorobenzene (PDCB). About 95% of the environmental releases of PDCB occurs during its use.EPA regulates the levels of PDCB in drinking water. The highest level of PDCB allowed in drinking water is 0.075 parts of per 1 million parts of water (0.075 ppm). The Occupational Safety and Health Administration (OSHA) has set a limit for PDCB of 75 ppm (75 parts of 1,4-dichlorobenzene per 1 million parts of air) in the workplace.

1,4-dichlorobenzene (1,4-DCB) is an environmentally hazardous substance. It is a chlorinated aromatic compound with a distinctive aromatic odour that is very strong at high concentrations. It is a white or colourless crystal at room temperature [1-2]. 1,4-Dichlorobenzene is practically insoluble in water; soluble in chloroform, carbon disulfide, benzene, and ether; and very soluble in ethanol and acetone. 1,4-Dichlorobenzene is noncorrosive, volatile, and combustible, and it is flammable when exposed to heat, flame, or oxidizers. When it is heated to decomposition, toxic gases and vapours such as hydrochloric acid and carbonmonoxide are released [3]. It is stable at room temperature under normal handling and storage in closed containers [4].

1,4-Dichlorobenzene has been used primarily as a space deodorant in products such as room deodorizers and toilet deodorant blocks and as a fumigant for moth control (accounting for about 35% to 55% of the 1,4dichlorobenzene produced) [5]. In 2007, it was used primarily as an intermediate in the production of polyphenylene sulfide, a plastic used in the electrical and electronics industries (52%) and in the production of 1,2,4trichlorobenzene [6]. Other uses of 1,4dichlorobenzene include use as a germicide or disinfectant; a soil fumigant; an insecticide for fruit borers and ants; a chemical intermediate in the production of various dyes, pharmaceuticals, and resin-bonded abrasives; an agent to control mould and mildew growth on tobacco seeds, leather, and some fabrics; and an extreme-pressure lubricant [7].Many studies show that 1,4-DCB can also be used as a surrogate for monitoring numerous other toxic chlorinated hydrocarbons such as dioxins from incinerators.

1,4-Dichlorobenzene is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals. Oral exposure to 1,4-dichlorobenzene caused tumours at several different tissue sites in mice and rats. Administration of 1,4-dichlorobenzene by stomach tube caused benign and malignant liver tumours (hepatocellular adenoma and carcinoma) in mice of both sexes and kidney cancer (tubular-cell adenocarcinoma) and mononuclear-cell leukaemia in male rats**.** It also increased the combined incidence of benign and malignant adrenal-gland tumours (pheochromocytoma) in male mice [8-9].

p-Dichlorobenzene is chosen as a representative of chlorobenzene(CBs) since it is one kind of the toxic organic compounds listed by Environmental Protection Agency as priority pollutants [10]. Additionally, CBs mainly exist in chemical industry wastewater and often mix with the organic and water solutions [11-13]. Recent studies have focused on the degradation of CBs in organic [14] or water solution [15]

CBs in waste water is degraded by various methods such as biodegradation [16-18], adsorption [19-20], incineration [21-22], catalytic hydride chlorination [23], and photocatalysis [24]. 1,4-dichlorobenzene (1,4-DCB) are used as solvents, chemical intermediates, deodorizers, and insecticides [25-26]. It is frequently used as a laboratory deodorant [27].

In the present work**,** a detailed study of determination of 1,4-dichlorobenzenein industrial waste water has been highlighted by spectrophotometric method .The method is based on the reaction of PDCB with N-PBHA in acidic media. The main advantage of the proposed method over the other methods is its higher sensitivity, short analysis time and higher the stability of formed complex. The method is also free from interference of many foreign species.

II. EXPERIMENTAL

***Instrument*:** "Systronics Spectrophotomter 1700" model was used for electronic spectral measurements with 10 mm matched quartz cells. A Hanna 8521 model pH meter was used for pH measurements.

***Reagents*:** All the chemicals used were of AR grade. All standard and sample solutions were made up with double distilled water.

***Preparation of solutions*:** Stock PDCB solution were prepared by dissolving 1gm of accurately weighed PDCB in 100ml of chloroform. Buffer solution with pH=10 for PDCB, was prepared by dissolving 70gm NH_4Cl in water and adding suitable amount of NH_4OH in 1lt distilled water. N-Phenyl-benzo-hydroxamic acid solution was prepared by dissolving 0.1gm in 100ml of chloroform. PDCB -PBHA complex was extracted in chloroform.4M hydrochloric acid solution was used to provide acidic medium.

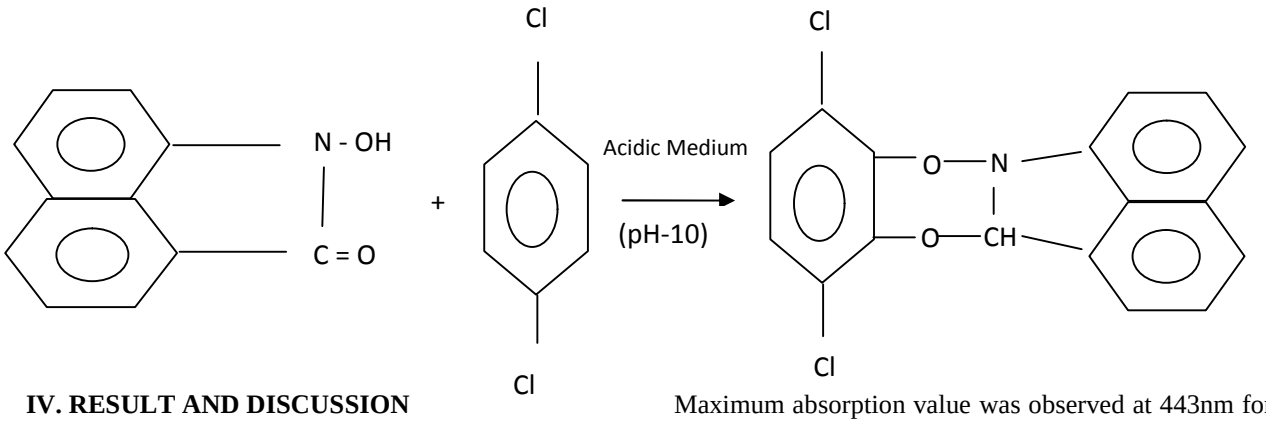
General procedure: The calibration curve was prepared by the following method:

It is done with a semi-micro burette. 1ml of each PDCB solution containing 0.0121-0.0512 µg/ml was transferred to a calibrating flask. This was followed by addition of 2ml of buffer solution, 1ml of N-Phenyl-benzo-hydroxamic acid in chloroform ,1 ml 4M HCl solution. Golden yellow colour was obtained. The absorbance was measured at 443nm for PDCB against reagent blank. Colour, Beer's law range, molar absorptivity, standard deviation, relative standard deviation and sandell's sensitivity are given in Table 1.

Table : 1 Parameters of N-PBHA and PDCB complexes.

S.No.	Parameters	PDCB
1	Colour	Golden Yellow
2	λ_{max} (nm)	443
3	Beer's law range (µg mL^{-1})	0.0121 – 0.0512
4	Molar Absorptivity (L $Mole^{-1}$ cm^{-1})	9.355×10^5
5	Standard deviation ±	0.0056
6	Relative standard deviation (%)	1.44
7	Sandell's sensitivity (µg/cm^2)	1.1×10^{-4}

III. EXPECTED REACTION



IV. RESULT AND DISCUSSION

Solubility: Significant differences in result existed by using different solvents. Table 2 shows that N PBHA has highest solubility in chloroform where as water resulted in lowest value**.** Thus chloroform was selected as a solvent for all experiments.

Absorption spectrum and calibration curve**:** After reaction, complex present in organic phase was scanned from 400nm to 600nm against reagent blank (Fig.1).

Maximum absorption value was observed at 443nm for the complex of PDCB with N-PBHA. Thus, 443nm was selected for absorption measurement throughout the experiments. Calibration plot of absorbance against concentration of PDCB at absorption maxima gave linear and reproducible graph in the concentration range of 0.0121 – 0.0512 µg/ml. The calibration curve is shown in Fig. 2.

Table 2: Solubility of N-PBHA in various solvents.

	Solvents	**Solubility (µg/ml)**
1.	Water	0.02
2.	n-Hexane	0.03
3.	Cyclohexane	0.08
4.	Carbon tetrachloride	0.16
5.	Benzene	1.66
6.	Toluene	0.29
7.	o-Dichlorobenzene	2.50
8.	Chlorobenzene	2.70
9.	**Chloroform**	**2.86**

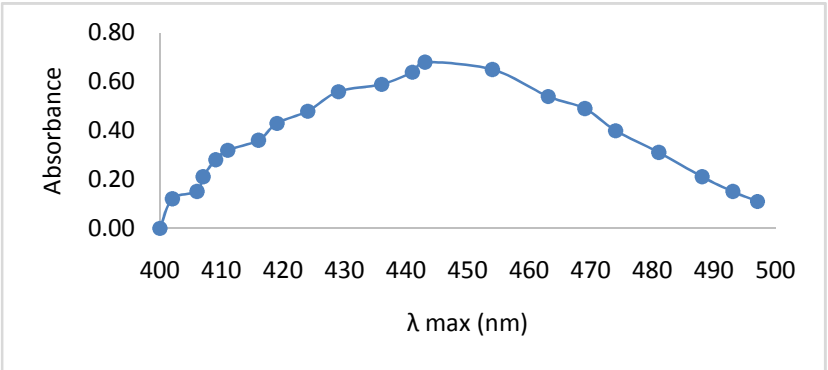


Fig. 1. Absorption spectra of PDCB.

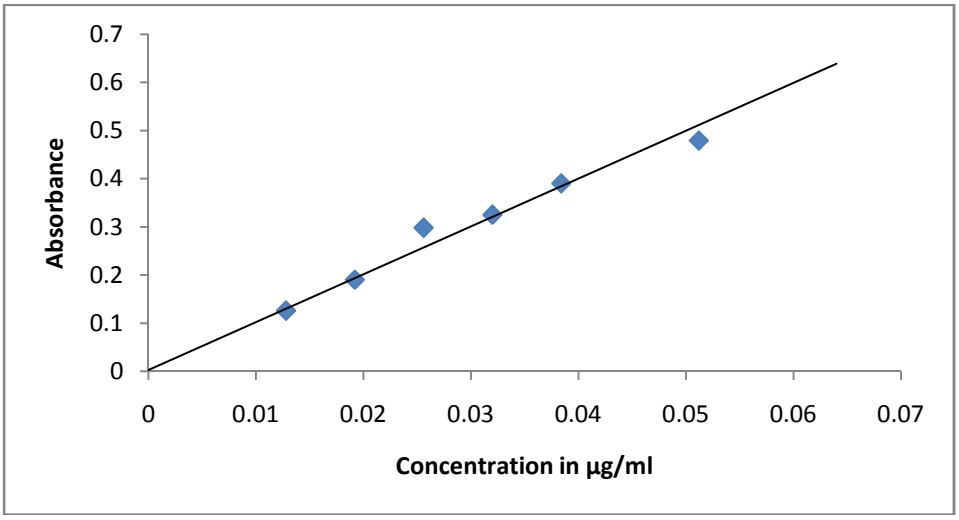


Fig. 2. Calibration curve for PDCB.

Effect of reagent concentration **:** The amount of N-PBHA was varied for determining its optimal concentration to a series of 1ml of PDCB. It was observed that by increasing the concentration of hydroxamic acid from 1ml (0.0001%) there was no change and a constant graph was obtained (Fig. 3). Thus1ml was used in experiment.

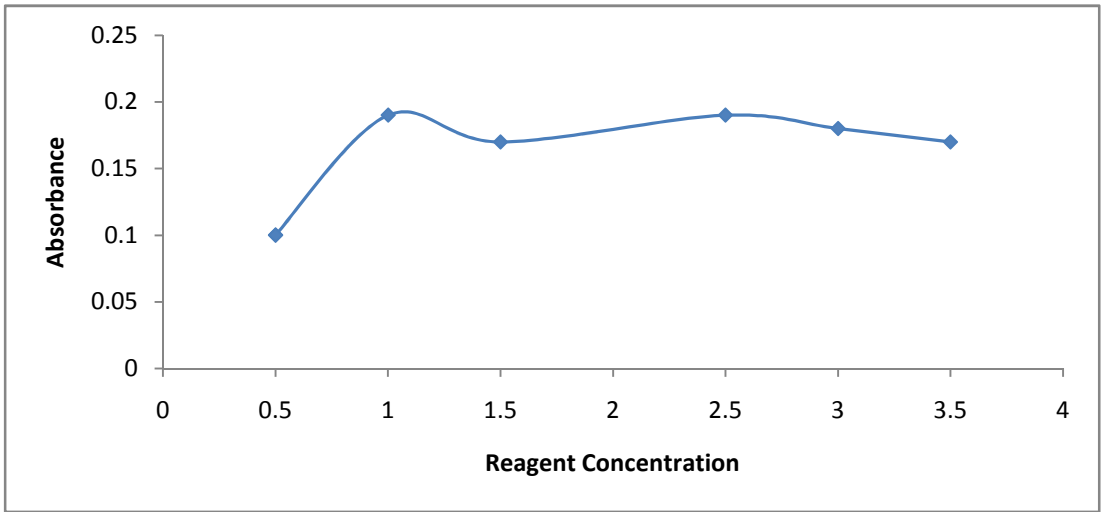


Fig. 3. Effect of reagent concentration.

Effect of time and temperature: The effect of temperature on colour stability and absorbance of the complex was studied over the temperature range of 10°C to 50°C. Room temperature (25°C) was found to be most suitable. On increasing temperature reaction stability and absorbance of complex decreases. Thus, all experiment were performed at room temperature .The colour developed immediately after addition of reactants and remained stable for several days (Fig. 4).

Effect of pH **:** Optimum condition was measured at pH range 1.0 – 10. Most effective result were obtained at pH-10 and by using 4M HCl. Increase or decrease in molarity results in fading of colour. This is shown in Fig. 5.

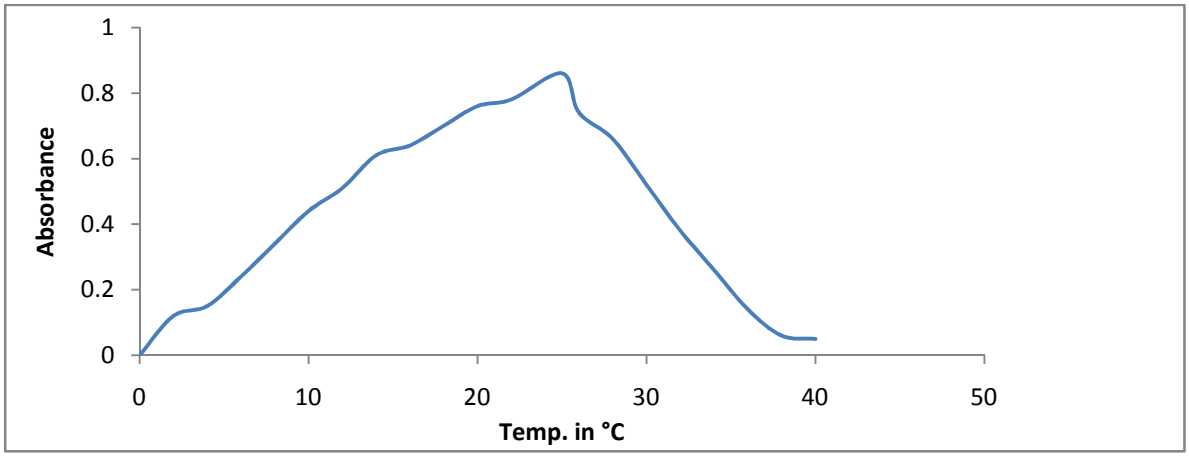


Fig. 4. Effect of temperature on PDCB.

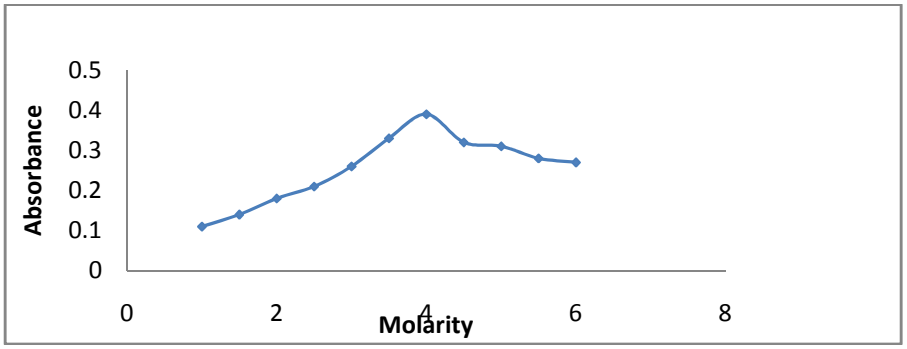


Fig. 5. Effect of molarity of acid on PDCB.

Order of addition of reagent **:** The order followed was - PDCB solution, PBHA solution in chloroform, HCl solution followed by distilled water. If the order is changed sensitivity decreases.

Effect of foreign species: To check the validity of the method, effects of several species commonly found alongwith PDCB solution on the reaction were studied. This was done by addition of known amount of these species to 3 µg PDCB prior to its analysis by the proposed method. The tolerance limits for various interfering species are shown in Table 3.

Table 3. Effect diverse ions on the determination of PDCB contents by N-PBHA.

Foreign Species	Tolerance level (µg/ml)
	PDCB
Methanol, Ethanol, Benzene	980
Toluene	310
Formaldehyde, aniline	270
o-nitrophenol	60
o-cresol, p-cresol, m-cresol	770
Hg^{2+}, Ca^{2+}, Pb^{2+}	780
Al^{3+}, Fe^{3+}	1150
PO^{4-}, SO^{4-}, CH_3COO^-	1380
S^{2-}	90

V. APPLICATION

In order to evaluate the analytical application of the method it was used for determination of PDCB in waste water of Union carbide industrial area (Bhopal). For analysis of real samples, some pretreatment is necessary.

All suspended particles should be removed by suitable procedures. Centrifugation was done. The samples were transferred in calibration flask and 0.5 ml of 0.2 mol^{-1} EDTA was added as masking agent and then the procedure reported was applied. The results are given in Table 4.

Table 4: PDCB contents in waste water.

Samples collection site	Amount of PDCB found in (µg/ mL)
W 1. At the entrance of UCIL	2.03
W 2. Electricity office near UCIL	1.22
W 3. Opp. Rajiv Bal Kendra	1.26
W 4. Near railway crossing	1.19
W 5. Near Ganesh temple at railway crossing	0.93
W 6. Near railway cabin Ayubnagar	0.86

VI. CONCLUSION

PDCB can be selectively detected and determined by spectrophotometric method with PBHA. It is found to be an effective new methodology for investigating PDCB. The reaction appeared to be quite universal since all the PDCB related spontaneously with absorption maximum around 443nm. Thus, this wavelength was of the choice for characterisation of PDCB. The reaction appeared to be very sensitive and therefore it is used as target for analysis of PDCB in waste water samples of Union Carbide factory area ,Bhopal. An added advantage of this method is that it is relatively cheap and easy to use. It should therefore be used to monitor the drinking water and other sources of water for levels of chlorobenzene in order to ensure public health protection and safety.

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