



RESEARCH ARTICLE

LOW COST METHOD FOR THE DETERMINATION OF PENTACHLOROPHENOL (PCP)

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ABSTRACT

A low cost method which based on the reaction of Pentachlorophenol (PCP) with concentrated nitric acid to form chloranil, which liberates iodine with potassium iodide, is described. The liberated iodine bleaches the violet colour of AZURE-B which is measure at 650nm. Beer's law is obeyed over the concentration range of 1-10 µg of PCP in final solution volume of 25 ml (0.04 - 0.4 ppm). The apparent molar absorptivity and Sandell's sensitivity were found to be $5.28 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $51 \times 10^{-5} \text{ µg cm}^{-2}$. The method has been satisfactorily applied to the determination of PCP in air, water, plant material, textile effluent and biological samples.

Key words: Pentachlorophenol (PCP), Spectrophotometric method, Chloranil, Sandell's sensitivity.

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INTRODUCTION

Pentachlorophenol (PCP) is a widely used non-inflammable insecticide and herbicide. PCP and Na-PCP are extremely toxic chemicals responsible for important soil and groundwater pollution, principally from wood-treatment plants, because chlorinated phenols are widely used as wood preservatives (Martin, 1968; Middaugh *et al.*, 1993). PCP is dangerous, when heated with nitric acid, and decompose to emit highly toxic fumes of chloranil (Sax, 1984). PCP is known for its toxicity and carcinogenicity (LD50- 0.20 g kg⁻¹ body weight of rats) and has adverse effect on several metabolic activities (Horstman *et la.*, 1989; Randerath *et al.*, 1994; Magda *et al.*, 1994). Human intake by inhalation and skin contact with contaminated surfaces. The main risks in acute poisoning are: hyperpyrexia, tachycardia, and a rise in the metabolic rate leading to death by cardiac arrest. In chronic exposure, the main risks are: skin, blood, neurological and respiratory disorders, porphyria, non-specific symptoms, and the possibility of cancer. Target organs are: skin, respiratory system, central nervous system (CNS), liver and kidneys, but especially metabolism at the cellular level (William *et al.*, 1982). Various instrumental techniques based on gas chromatography (Rodriguez and Cela, 1997; Hexinxu *et al.*, 1998), gas liquid chromatography (Gaspar *et al.*, 1975), thin layer chromatography (Sherma and McGinnis, 1995), HPTLC (Mahmood *et al.*, 1996), HPLC (Pocurull *et al.*, 1995),

supercritical fluid extraction (Mayer *et al.*, 1996), electrophoresis (Turnes *et al.*, 1996), isotope dilution mass spectrometry (Wade *et al.*, 1978) differential pulse polarography (Shi, 1995) etc. are reported for its determination. A number of spectrophotometric methods using different reagents such as 4-aminophenazone (Benize, 1963), fuming nitric acid (Steven and Richardson, 1979), methylene blue, crystal violet (Das and Gupta, 1994) and leucocrystal violet (LCV) (Agrawal and Gupta, 1998) etc. have been reported for the determination of PCP. While colour developed in the method using methylene blue, and crystal violet are less stable, reagent LCV is very costly. Here a new simple and sensitive method for the quantitative determination of PCP is reported. On warming PCP with concentrated nitric acid PCP is converted to chloranil (Venkataraman, 1952), which liberates iodine from potassium iodide. The liberated iodine bleaches the blue colour of Azure B dye (Shivhare and Gupta, 1991). The intensity of the colour was measured at 650 nm. The method has been applied for the determination of PCP in air, polluted water, biological samples, industrial effluents and plant foliages.

EXPERIMENTAL

Apparatus: A Systronics 106 digital spectrometer and a Systronics 335 digital pH meter were used. For airs sampling midget impingers of 35ml capacity were used for flow rate was controlled by a PIMCO make calibrated rotameter.

Reagents: All the chemicals used were of analytical-reagent grade and distilled water was used for dilution of reagents and samples.

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Pentachlorophenol (PCP, G.S. Chemicals, Mumbai): A stock solution of 1 mg ml^{-1} was prepared dissolving 10 mg of purified PCP in 10 ml of methanol. Working standards were prepared by appropriate dilution of stock solution with water.

Potassium iodide (E. Merck, Mumbai): 0.2 % aqueous solution was used.

Azure B (Stuttgart, vv. Germany): 0.5% aqueous solution was used.

Acetate Buffer: Buffer solution was used of pH 4.

Hydrochloric acid: 1M aqueous solution HCl was used.

PROCEDURE

Preparation of calibration curve: An aliquot of working standard solution containing 1-10 μg of PCP was taken in a 25 ml calibrated tube and two drop of concentrated nitric acid were added to it. The solution was warmed for two minutes will the appearance of yellow colour which indicated the formation of chloranil. The solution was cooled to room temperature and 2 ml of potassium iodide was added. The yellow colour intensifies, indicating the liberation of iodine. The mixture was gently shaken after the addition of 1 ml of Azure B and 2 ml of acetate buffer solution of pH 4 and the reaction mixture shaken for 2 minutes. The volume was made up to 25 ml with double distilled water. The absorbance of the resulting solutions were measured at 650nm against the corresponding reagent blank.

Determination of pentachlorophenol (PCP) In polluted water: 100 ml of river water sample, which receives effluents from textile mill, was taken. It was filtered and then a known amount of PCP was added and determined by the proposed and the reported method (25) (Table-1).

In plant foliage: Preparation of column - silica gel (100-200 mesh) for column chromatography was used for the preparation of column. A 25 ml glass column (internal diameter 9-10 mm) was taken in which a glass wool pad was put near the stopcock. 5 gm. of silica gel was kept in glass column and washed with water. For each test a fresh column was used (Thompson *et al.*, 1994). Various samples of plant foliage of cotton, sugarcane, beans were collected from field, where PCP was used as herbicide. 10 mg samples were crushed and blended in a mixer with two 10 ml portions of methanol and filtered. The filtrate was passed through silica gel column (10 x 1 cm) to remove chlorophyll and other interfering materials. The column was washed with 10 ml of methanol. The washing was collected in a 50ml volumetric flask and aliquots were analysed as described above according to the reported method (Das and Gupta, 1994) (Table-1).

In textile industry effluents: Effluents from textile mill were collected and filtered using Whatman filter paper No .40. Aliquots were analysed by the proposed and reported method (Das and Gupta, 1994) (Table -1).

In biological samples: The PCP has been reported to be present in blood and urine after its exposure (Aldrige, 1944). Hence the method was applied for its determination in blood and urine sample to check its applicability on biological samples. PCP free samples were taken and a known amount of PCP added to them and analysed after deproteinization by

trichloroacetic acid by the proposed and reported method (25). The recoveries were found to be 96-98 % (Table -1).

In air

5-25 μg of PCP was vaporized by gentle heating in impinger and vapour were absorbed in another impinger containing 10 ml of 10% methanol as absorbing medium and connected to a source of suction. The air was sampled at the rate of 0.5-1.0 l/min for 10-30 min. The aliquots of absorbing solution were then analysed by the proposed and reported method (25). The recoveries varied from 96 - 98% (Table -1).

RESULTS AND DISCUSSION

Spectral characteristics: This method involves the liberation of iodine by the reaction of PCP with potassium iodide in an acidic medium. The liberated iodine bleaches the blue color of Azure B and absorbance of the solution is measured at 650 nm. This decrease in absorbance is directly proportional to the PCP concentration. The absorption spectrum of colored species of Azure B is presented in Figure 1 & 2 and reaction system is presented in Scheme A.

Adherence to Beer's Law, Molar absorptivity and Sandell's sensitivity: The colour system obeys Beer's law over the concentration range of 2-10 μg of PCP per 25 ml of the final solution (0.04 - 0.4 ppm) at 650 nm (Fig-2). The apparent molar absorptivity and Sandell's sensitivity were found to be $5.28 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $51 \times 10^{-5} \mu\text{g cm}^{-2}$ respectively.

Scheme – A. Colour reaction of pentachlorophenol (PCP)

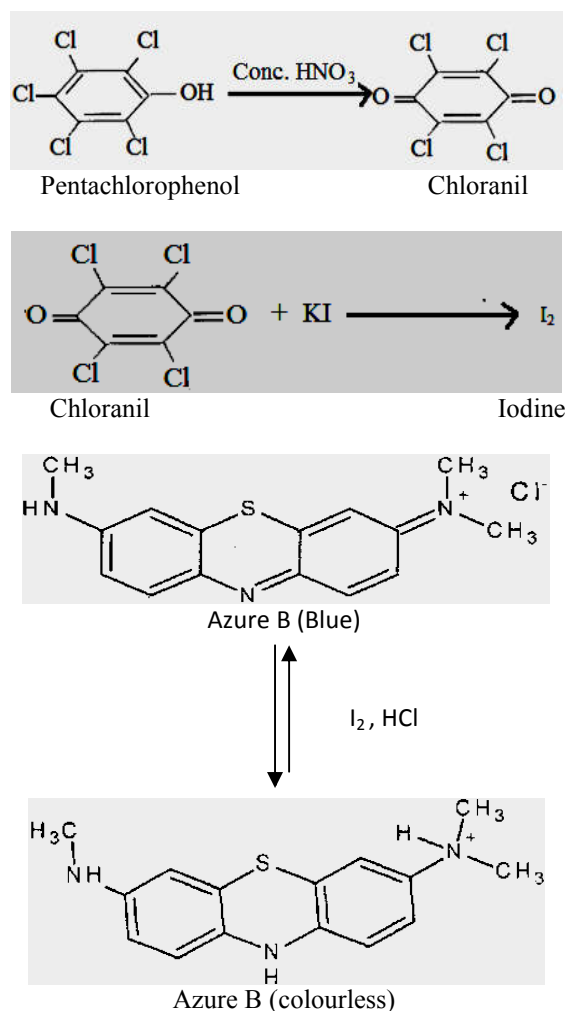


Table 1. Determination of PCP in different samples by the proposed and reported method

Sample volume or mass	PCP originally found	PCP added (µg)	Total PCP Found (µg)	% of recovery
Polluted water (100 ml)				
A	2.96 (2.81)	5	7.80(7.60)	98.1(97.4)
B	3.52(3.42)	5	8.36(8.19)	98.2(97.3)
C	4.58(4.50)	5	9.43(9.26)	98.5(97.5)
Plant foliages (100g)				
Sugar cane				
Cotton	0.450(0.460)	6	6.340(6.266)	98.3(97)
Beans	0.184(0.174)	6	6.091(6.050)	98.5(98)
Textile effluent(1ml)	0.146(0.136)	6	6.072(6.043)	98.8(98.5)
Biological samples				
Blood (2ml)				
A	1.110 (0.989)	5	6.012 (5.821)	98.4(97.2)
B	-	3	2.94(2.93)	98.0(97.6)
C	-	5	4.92(4.91)	98.4(98.2)
Urine (2ml)				
A	-	7	6.91(6.87)	98.7(98.1)
B	-	3	2.89(2.86)	96.6(95.3)
C	-	5	4.90(4.80)	98.0(96.0)
Air (0.5 -1 l/min.)				
A	-	7	6.89(6.81)	98.4(97.2)
B	-	5	4.81(4.79)	96.2(95.8)
C	-	7	6.82(6.80)	97.5(97.2)
	-	10	9.81(9.78)	98.1(97.8)

Table 2. Effect of diverse ions in the determination of PCP (2 µgml-1)

Foreign ions	Tolerance Limit (ppm)	Foreign ions	Tolerance Limit (ppm)
Fe ³⁺ , Cd ²⁺	400	NO ₃ ⁻ , CO ₃ ²⁻	800
Ni ²⁺ , Cu ²⁺	550	Ethion	1000
Bi ³⁺ , Al ³⁺	500	Malathion	650
PO ₄ ³⁻ , SO ₄ ²⁻	710	DDT, BHC	200

Table -3 Comparison of Spectrophotometric Method for the Determination of PCP with Proposed Method

S.No.	Reagent	Medium /pH	λmax. (nm)	Beer's law range (ppm)	Remarks
1.	Rhodamine-B	Acidic (1.5-2.5)	555	0.04-0.4	Complex stability 2 hrs, less sensitive.
2.	Leuco crystal violet (LCV)	Acidic (4.5-5.5)	592	0.0004- 0.064	Rapid, sensitive and non extractive but highly expensive and costly.
3.	Methylene blue	pH 8.5	620	1-100	Require primary treatment of reagent, stability one week.
4.	Azure-B (proposed method)	Acidic (4.02)	650	0.04-0.4	Simple sensitive, higher stability, less interference.

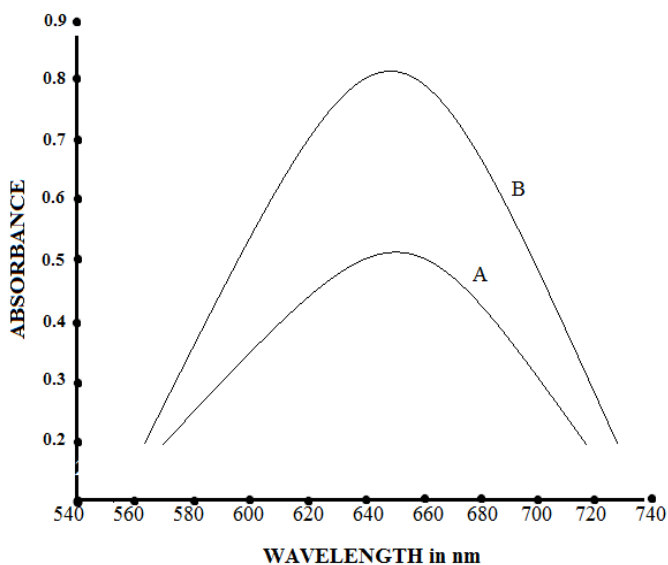


Fig. 1. Absorption spectra of the dye A-Concentration of PCP in µg/25ml B-Reagent Blank

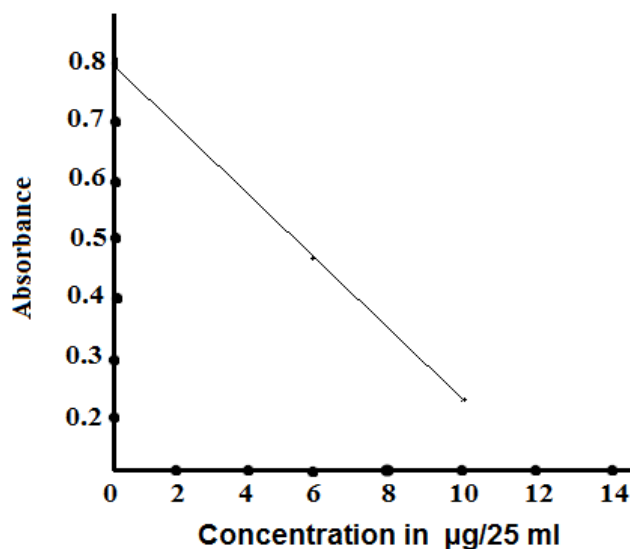


FIG-2 Calibration curve for determination of PCP

Effect of reagent concentration: The effect of iodide concentration and acidity on the reaction system is studied with $2\mu\text{gml}^{-1}$ PCP. The oxidation of iodide to iodine by PCP is effective in the pH range 1.0-1.5, which can be maintained by adding 1 ml of 1 M HCl in a final volume of 25 ml. The liberation of iodine from potassium iodide in an acidic medium is quantitative. It is found that 1 ml of 0.2 % KI and 1 ml of 1M HCl are sufficient for the liberation of iodine from iodide by PCP. A 0.5 ml of 0.5 % Azure B is used for subsequent decolorization. Constant and maximum absorbance values are obtained in the pH range of 4 ± 0.2 . Hence the pH of the reaction system is maintained at 4 ± 0.2 throughout the study. This can be achieved by the addition of 2 ml of 1 M acetate buffer solution in a total volume of 25 ml the maximum absorbance is obtained instantaneously and requires no heating under the reaction conditions. Under the optimum reaction conditions, Azure B reaction systems are found to be stable for a period of 5 hours.

Reproducibility: Reproducibility of the method was accessed by analysis $5\mu\text{g}$ of PCP per 25 ml for a period of seven days. The standard deviation and relative standard deviation were found to be ± 0.0069 and 1.25% respectively.

Effect of foreign species: The effect of various species on the determination of PCP was studied. The tolerance limit value of different foreign species in the solution containing $5\mu\text{g}$ per 25 ml of PCP is presented in Table-2. Other phenols and chlorophenols do not interfere, since they do not form chloranil under the present reaction condition. The anions SO_4^{2-} , PO_4^{3-} and metal ion Zn^{2+} , Ca^{2+} , Fe^{3+} , Bi^{2+} did not interfere with the method. Other compounds which can liberate iodine from potassium iodide under the present experimental condition are likely to be interfering.

Colour reaction: The colour reaction involves the following steps (Scheme - A)

- A. Formation of chloranil by brief warming of PCP with concentrated nitric acid.
- B. Iodine liberates as a result of reaction between potassium iodide and chloranil formed.
- C. Liberated iodine oxidizes of azure -B.

Application

The method has been successfully applied for the determination of PCP in polluted water, air, plant foliages, textile industry effluent and biological samples

Conclusion

The reagents provide simple method for the spectrophotometric determination of PCP. The developed method does not involve any extraction step and hence the uses of organic solvents, which are generally toxic, are avoided. The developed method does not involve any stringent reaction conditions and offers the advantages of high stability of the reaction system for Azure B (more than 5 hours). The proposed method has been compared with other spectrophotometric method reported for PCP (Table -3) and found to be simple and sensitive than most other methods .

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