

Spectroscopic Technique Used for the Identification of Pentachlorophenol in Environment

Abstract

The simple spectroscopic method is used for the determination of penta chloro phenol (PCP). This technique is based on the reaction of pentachlorophenol with conc. Nitric acid to form chloranil, which liberates iodine with potassium iodide. The liberated iodine forms a water soluble blue complex in the presence of starch having absorption maximum at 570nm. Beer's law is obeyed over the concentration range of 3.7 – 27µg of PCP in a final solution 100ml (0.035 – 0.35ppm) and has molar absorptivity and sandell's sensitivity values of $8.4 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.000457 \text{ igcm}^{-2}$ respectively. This technique has been used to determine pentachlorophenol in environmental samples.

Keywords: Pentachlorophenol, Nitric Acid, Chromatography Starch.

Introduction

Pentachlorophenol is a widely used insecticide and herbicide. It is used as a wood preservative for the control of termite¹. It is also used as a fungicide for the protection of timber from fungal rots and insects. PCP is strongly phytotoxic and used as a general herbicide for many crops². PCP is known for its toxicity and carcinogenicity and has adverse effect on several metabolic activities³. PCP has been classified as a B₁₂ probable human carcinogen by US EPA based on sufficient evidence from animal toxicity studies⁴. The observed symptoms of toxic effect in human beings include dermatitis, loss of appetite, respiratory difficulties, hyperpyrexia⁵.

Several instrumental methods using gas chromatography⁶ gas liquid chromatography⁷ thin layer chromatography⁸ HPLC⁹ flow injection analysis¹⁰ solvent extraction¹¹ etc are reported for the determination of penta chlorophenol.

A number of spectroscopic methods using different reagents such as fuming nitric acid¹² Methylene blue¹³ crystal violet¹⁴ rhodamine-B¹⁵ safranin¹⁶-O CTAB (Cetyltrimethyl ammonium bromide)¹⁷ etc. have been reported. Here a simple and sensitive method for the quantitative determination of PCP is reported. On warming with conc. nitric acid PCP is converted to chloranil¹⁸, which liberates iodine from potassium iodide. The liberated iodine forms a water soluble blue complex with starch having absorption max. at 570nm.

Experimental

Apparatus

A Toshniwal spectrophotometer TVSP-25 model and a systronics 331 digital pH meter were used for air sampling midge impingers of 45ml capacity were used, flow rate was controlled by a PIMCO make calibrated rotameter.

Reagents

All the chemicals used were of the best quality. Double distilled water was used throughout the experiment. A 2mg/ml solution of penta chlorophenol (G.S. Chemicals Mumbai) was prepared by dissolving 12mg of purified PCP in 12ml of methanol. Working standard solution was prepared by appropriate dilution of the stock. A 0.1% aqueous solution of potassium iodide was prepared and conc. nitric acid was used. Starch solution – 150mg amount of soluble starch was made into a paste with a few drops of hot water and diluted to 150 ml using nearly boiling water.

Procedure

An aliquot containing 2.5 to 25µg of PCP was taken in a 100ml calibrated flask and 2 drops of concentrated nitric acid were added to it and the solution was warmed for 4 minutes in a boiling water bath till the appearance of yellow colour which indicated the formation of chloranil. The



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solution was cooled at room temperature and 3ml of potassium iodide was added.

The yellow colour intensifies, indicating the liberation of iodine. The mixture was gently shaken with the addition of 0.3ml of starch solution. The contents were diluted to the mark with water and the absorbance measured at 570nm against a reagent blank.

In air

5-25µg of PCP was vaporized by gentle heating in impinger and vapour were absorbed in another impinger containing 12ml of 12% methanol as absorbing medium and connected to a source of suction. The air was sampled at the rate of 0.5 – 1.0 l/m for 10-30 minutes. After absorption of PCP, 2drops of conc. nitric acid were added to it and solution was warmed for 3 minutes will the appearance of yellow colour which indicated the formation of chloranil. The solution was cooled to room temperature and 2ml of potassium iodide and 0.2ml of starch solution were added and mixture set aside for a further 4 minutes. The contents were diluted to the mark with water and the absorbance measured at 570nm against a reagent blank. The aliquots of absorbing solution were analysed by reported method also (15) Table 2.

Result and Discussion

Spectral Characteristics

The absorption spectrum of the colour system showed maximum absorbance at 580nm. All the spectral measurements were carried out against demineralised water since the reagent blank showed negligible absorbance at this wavelength.

Effect of Time & Temperature and pH

Maximum absorbance value was obtained in the pH range of 1-2. Time period 5 minutes was sufficient for iodine liberation and a further 2 min, was necessary for complete colour development. The effect of temperature on the colour reaction and the stability of the dye was studied. It was found that a temperature of between 20 – 32°C was suitable for the reaction.

Effect of Reagent Concentration

The effect of various reagent concentration were studied. It was found that two drops of nitric acid were sufficient for the formation of chloranil, 2.0ml of 0.1% KI was sufficient for liberation of iodine and 0.2ml of 0.1% starch solution was sufficient for the colour reaction starch solution was prepared daily.

Table 2. Application of the method for determination of PCP in different samples by the proposed and reported method

Sample volume or mass	PCP originally found (µg)	PCP added (µg)	Total PCP found (µg)	% of recovery
Polluted water (100ml)				
A	2.50 (2.46)	4	7.40 (7.31)	99.19 (98)
B	3.62 (3.52)	4	8.42 (8.33)	97.67 (97.76)
C	3.71 (3.60)	4	8.54 (8.54)	98.04 (99.30)
Plant Foliages (100g)				
Sugar cane	0.442 (0.45)	5	5.325 (5.340)	97.85 (97.98)
Beans	0.150 (0.145)	4	5.120 (5.072)	99.41 (98.58)
Biological samples Blood (2ml)				
A	-	2	2.99 (2.95)	99.6 (98.3)
B	-	4	4.80 (4.79)	96.0 (95.8)
C	-	6	6.89 (6.87)	98.4 (98.14)

Adherence to Beer's laws, Molar Absorptivity and Sandell's Sensitivity

The colour system obeys Beer's law over the concentration range of 2.5 – 25µg of PCP per 100ml of final solution (0.025 – 0.25 ppm) and 5 – 25µg (0.05-0.25 ppm) in air at 580nm. The molar absorptivity and Sandell's sensitivity were found to be $9.2 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.000287 \text{ µg cm}^{-2}$ respectively.

Reproducibility

The reproducibility of the method was assessed by carrying out seven replicate analysis of a solution containing 15 µg of PCP.

The standard deviation and relative standard deviation of absorbance values were found to be ± 0.0067 and 1.21% respectively.

Effect of Foreign Species

The effect of various foreign species on the determination of PCP was studied, 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 ions Zn^{2+} , Ca^{2+} , Fe^{3+} , Bi^{2+} did not interfere with method. The tolerance limit value of different foreign species in the solution containing 5 µg of PCP are presented in Table 1.

Application of the Method

The method has been applied for the determination of pentachlorophenol in polluted water, air and biological samples.

In Polluted Water

Polluted water sample from nearby run off agricultural field was taken where PCP was used as a herbicide. It was filtered and then a known amount of PCP was determined by the proposed and the reported method (15) Table 2.

Table 1. Effect of Foreign Species (Concentration of PCP = 5µg per 100ml)

Foreign species	Tol. limit (ppm)	Foreign species	Tol. limit (ppm)
SO_4^{2-} , PO_4^{3-}	2345	Phorate	945
NO_3^- , CO_3^{2-}	1800	DDT, BHC	210
Zn^{2+} , Al^{3+}	945	o-Cresol	120
Co^{2+} , Ca^{2+}	450	m-Cresol	110
Co^{2+} , Fe^{3+}	1430		
Pb^{2+} , Sn^{4+}	175		
Ethan	1100		
Malathion	940		

* Tolerance limit is the amount of interference that causes an error of $\pm 2\%$.

Urine (2ml)				
A	-	3	2.78 (2.75)	99.6 (98.6)
B	-	4	4.95 (4.90)	96.0 (95.0)
C	-	6	6.72 (6.71)	98.4 (95.85)
Air 0.5 – 11/min Flow rate				
A	-	4	4.88 (4.87)	97.6 (97.4)
B	-	6	6.75 (6.75)	96.4 (96.4)
C	-	8	8.91 (8.90)	99.0 (98.8)

Figure in parentheses are reported by method Ref. (15).

In Biological Samples

The PCP has been reported to be present in blood and urine after its exposure. Hence samples of blood deproteinised with trichloroacetic acid were taken and analyzed by proposed and reported method (15) Table 2.

Determination of PCP in Plant foliage

A 10 x 1ml glass column containing silica gel (100 – 200 mesh) was prepared and washed with water. Various samples of foliage of sugarcane and beans were collected from field where PCP was used as herbicide. The samples were weighed and crushed with portion of methanol (10ml) and filtered. The filtrate was greenish yellow due to the presence of chlorophyll and other pigments. The filter was then passed through a silica gel column to remove coloured organic matter. The column was washed with 10ml of methanol and washing was collected with a 50 ml volumetric flask. Then aliquots were analyzed as described above and by the reported method (15) Table.2.

Conclusion

This method has been found to be more simple, sensitive and cheaper in cost than the other methods. This method gives more satisfactory results when applied for the determination of PCP in various environmental and biological samples.

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Endnotes

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