

Separation and Estimation of Pentachlorophenol in Treated Wood

COLONEL Y. P. MISRA, S. P. SINGH DHAKAREY, R. K. JAISWARA AND SUSHMA GUPTA

Chief Inspectorate of General Stores, Kanpur

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The paper discusses and highlights the results of investigations undertaken by the authors wherein they have established a more simple method for the separation and determination of pentachlorophenol or its sodium salt from wood extractives, other preservatives and its colorimetric determination.

PENTACHLOROPHENOL and its sodium salt is used extensively as wood preservative due to its excellent fungicidal properties. Several methods have been proposed for its determination from preserving solution. Haskins¹, and Wallin² have described the estimation of pentachlorophenol colorimetrically with methylene blue in alkaline medium. Laamanen³, has reported colorimetric micro-determination of pentachlorophenol with tetramethyl base. Reynolds⁴, Keen⁵ and Harlow⁶ have described volumetric method for its determination.

Different formulations have been described in various standards to increase fungicidal activity of preservatives by incorporating of other chemicals e.g. zinc and copper naphthenates, disodium octaborate and *Y*-benzene hexachloride along with pentachlorophenol. Fire retarding agents such as zinc, chromium salts and diammonium phosphate are also used together with pentachlorophenol for the treatment of plywood. It has been observed that during extraction of pentachlorophenol with organic solvent, some phenolic compounds of wood and other preservatives are also extracted, therefore, it is not possible to estimate pentachlorophenol from treated wood without the separation of other preservatives by direct method as described earlier. The method described in BWPA standard 7 which involves refluxing and steam distillation to separate pentachlorophenol from treated wood is time consuming. The lower chlorophenols and other steam volatile phenolic compounds of wood extractives are also not separated by this method. Very recently Williams⁸ have described a method for the extraction and determination of pentachlorophenol from softwood and preservative solutions. He has separated pentachlorophenol from wood extractives and chlorophenols by absorption onto Bio-Rad AG-2-X-8 anion exchange resin and estimated spectrophotometrically with 4-aminophenazone.

In the present communication we have described a more simple method for the separation of pentachlorophenol from other preservatives and wood extractives and its colorimetric determination. Pentachlorophenol is extracted from wood shavings with ethyl alcohol and glacial acetic acid mixture (90 ml+

10 ml) and separated from other chemicals by thin layer chromatographic technique and then estimated colorimetrically with tetrabase.

Experimental

All the chemicals used were either of Analar BDH/S. Merck quality.

5.0 g shavings (containing about 2 mg of pentachlorophenol) of a sample of treated wood were extracted with 50 ml of ethyl alcohol and acetic acid mixture (90 ml ethyl alcohol+10 ml glacial acetic acid) by heating on a hot plate for ten minutes. The extracted pentachlorophenol in alcohol was filtered through Whatmann filter paper No. 41. For complete extraction of pentachlorophenol this operation was repeated two times. Finally the volume was made upto 100 ml by evaporation of alcohol or less if the concentration of pentachlorophenol is less than two milligrams.

Chromatographic plates (20×20 cm) were prepared by pouring a slurry of silica gel of particle size 75U (calcium sulphate 13.0 percent) in distilled water containing 1 percent oxalic acid on glass plates. The plates were left at room temperature overnight and activated at 110° for 1 hr; the average coatings of silica gel was 50 mg/cm².

The extracted (0.5 ml to 1.0 ml) solution of pentachlorophenol was spotted on silica gel plate. The chromatogram was developed in benzene solvent till the solvent front had advanced upto 15 cm. The plate was dried at room temperature and the presence of pentachlorophenol identified as orange colour spots by spraying hot concentrated nitric acid with glass atomizer. The *R_f* value was determined by measuring the lengths of solvent front and the position of the orange colour spots of pentachlorophenol. The spots were scrapped off with a spatula and extracted thoroughly with benzene. This operation was also done with standard solutions of pentachlorophenol.

Benzene solvent was evaporated by heating on water bath. Dried pentachlorophenol was treated with 0.5 ml of concentrated nitric acid and heated

on water bath for two minutes. It was then cooled and four drops of saturated solution of urea and 10 ml of saturated ammonium acetate solution were added (pH 7-7.5).^{*} To this solution 3 ml of 0.5 percent tetrabase solution was added and the precipitate was dissolved in 3 ml of glacial acetic acid. This solution of bluish green colour was filtered through Whatmann filter paper No 41 and optical density was measured at 640 m μ with a colorimeter. The results are tabulated below.

Sl. No.	Pentachlorophenol standard solution	Optical density at 600m μ	Pentachlorophenol from treated wood	Optical density at 600m μ
1.	1.25 mg	0.22	1.25 mg	0.23
2.	2.00 mg	0.36	2.00 mg	0.35
3.	2.50 mg	0.44	2.50 mg	0.46
4.	3.00 mg	0.55	3.00 mg	0.53

Standard solution of pentachlorophenol was prepared by dissolving 0.5 g of pure pentachlorophenol in 100 ml of pure ethyl alcohol.

0.5 ml of above solution \equiv 2.5 mg of PCP. Calibration graph was plotted with optical densities against different concentrations (in mg) of standard solution of pentachlorophenol.

Results and Discussion

It has been observed that oxidized pentachlorophenol forms green colour solution or precipitate with tetrabase (tetra methyl *pp'* diamino diphenyl methane) in presence of wood extractives and other preservatives. Deters,⁸ and Petrowitz,⁹ have reported the separation of pentachlorophenol from other lower chlorophenols by thin layer chromatography technique. We have observed that penta-

chlorophenol can also be separated from wood extractives and other preservatives by this technique. It has been found that pentachlorophenol after separation from wood extractives and other preservatives by thin layer chromatography method, forms beautiful orange colour spots with hot concentrated nitric acid on silica gel plate due to its oxidation to chloronil. The formation of chloronil as oxidation product of pentachlorophenol with hot nitric acid has been reported by Giese and Dechmann¹². These orange colour spots when extracted and treated with tetramethyl *p-p'* diamino diphenyl methane in presence of ammonium acetate (pH 7-7.5) forms a bluish green colour solution and not green colour as in the presence of impurities. The R_f value was calculated for pentachlorophenol and found to be 0.68 where as for inorganic preservatives it is less than 0.05. Wood extractive forms brown spots within the area of two cms. at the bottom on the silica gel plate. The results of pentachlorophenol extracted from the treated wood are quite similar to that of standard solution. This method is applicable for the determination of pentachlorophenol in treated wood within the range of 1.25 mg to 2.5 mg of pentachlorophenol for good results.

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* Tetra base solution was prepared by dissolving 5.0 g of tetramethyl *p-p'* diamino diphenyl methane and 20 g of citric acid in 20 ml of water and then diluted to 1000 ml.