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## DETECTION OF PETROLEUM OIL DILUENTS IN COAL TAR CREOSOTE BY THIN-LAYER CHROMATOGRAPHY

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## SUMMARY

A thin-layer chromatographic method is described for the detection of four types of petroleum oils used as diluents in creosote. These oils vary widely in aromatic and paraffinic content. The presence of these oils can be demonstrated down to a level of 0.25 % in creosote. The indicator,  $\alpha$ -cyclodextrin followed by iodine fumes, should be useful in other applications where differentiation between aromatic compounds and hydrocarbons is desired.

## INTRODUCTION

In the United States, high temperature-type coal tar creosote is the most widely used material for the preservation of wood used for heavy construction. For land uses, such as for railroad crossties, blends of creosote with as much as 50 % byproduct petroleum fuel oils are recognized in American Wood-Preservers' Association (AWPA) Specifications and higher ratios of petroleum are used by some railroad companies. For marine uses, however, the effectiveness of creosote is reduced sharply by the presence of petroleum<sup>1</sup>. An important objective of specifications for marine-grade creosote is to restrict the presence of petroleum to the lowest practical limit. It is recognized that, in a commercial treating plant where a charge of marine piling treated with "pure" creosote may follow a charge of crossties treated with a creosote-petroleum blend, some contamination of the marine-grade creosote by oil is unavoidable. At present, there is no agreement as to what constitutes a reasonable tolerance.

Several methods for the determination of petroleum in creosote have been reported. Results from the distillation and specific gravity test<sup>2</sup> vary with the nature of the petroleum. Several methods have been based on differences in the solubility of aromatic and saturated compounds<sup>3</sup>. The U.S. Naval Civil Engineering Laboratory described a test by column chromatography<sup>4</sup>. Infrared techniques have been reported<sup>5,6</sup>. For one reason or another, none of these methods have come into extensive use, especially with creosotes containing low levels of petroleum oil. For use at treating

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plants, the most desirable method would be one that could obtain results quickly and be conducted with moderately priced equipment.

Since creosote is composed of a wide variety of compounds, perhaps 500, and contains liquid and solid aromatic hydrocarbons, we felt that thin-layer techniques could be used to simplify the separation process by holding the aromatics back and permitting a fraction of the petroleum additive to be positioned nearer a selected solvent front.

## EXPERIMENTAL

### *Materials*

A medium-residue creosote that had been carefully analyzed by standard American Wood-Preservers' Association methods and used in trials of additional test methods was selected as a typical commercial creosote.

Four petroleum oils were selected for blending with creosote. Two were heavy fuel oils of the types commonly used in blends for treating crossties. One was relatively low and the other very high in aromatic hydrocarbons. The other two petroleum oils were distillates that are used in preparing pentachlorophenol solutions for treating products such as poles and lumber having higher cleanliness requirements than crossties. These two oils differed widely in their content of hydrocarbons. Solutions were prepared by weight to contain 0.25, 0.5, 1, and 2 % petroleum diluent in the creosote.

30 g of Silica Gel H (Brinkman Instruments, Inc., Westbury, N.Y.) powder were shaken with 70 ml of water and spread on standard 20 cm square glass plates to give a layer 25  $\mu$  thick.

The developing solvent was Chromatoquality reagent *n*-hexane (Matheson, Coleman & Bell, East Rutherford, N.J., CQ 5093).

All samples were diluted with reagent-grade toluene for spotting.

Indicators were  $\alpha$ -cyclodextrin (Applied Science Laboratories, Inc., State College, Pa.)<sup>7</sup> followed by iodine fumes obtained by passing air through a 150 mm drying tube which contained iodine crystals.

1  $\mu$ l microcap pipettes were used.

### *Procedure*

50 mg samples were weighed and diluted with 1 ml of reagent-grade toluene. The air-dried plates were activated by heating for 1 h at 105°. The diluted samples were spotted about 20 mm from the bottom of the plates. To reduce the size of the spots, each sample was spotted five times in the same place with the 1  $\mu$ l pipettes to give a sample loading of 5  $\mu$ l. Samples were: creosote alone; creosote containing 0.25, 0.5, 1, and 2 % petroleum diluent; and diluent alone. Plates were developed in glass chromatography jars with *n*-hexane as the solvent. The solvent was allowed to ascend to within 1 in. of the top of the plate. At 25°, development time was less than 1 h.

After development, the plates were sprayed with  $\alpha$ -cyclodextrin. The plates were then allowed to air dry and fumed with iodine. A white spot against a brownish-purple background appeared near the solvent front for the samples containing the petroleum oils. The spots for the aromatic compounds in the creosote were brown.

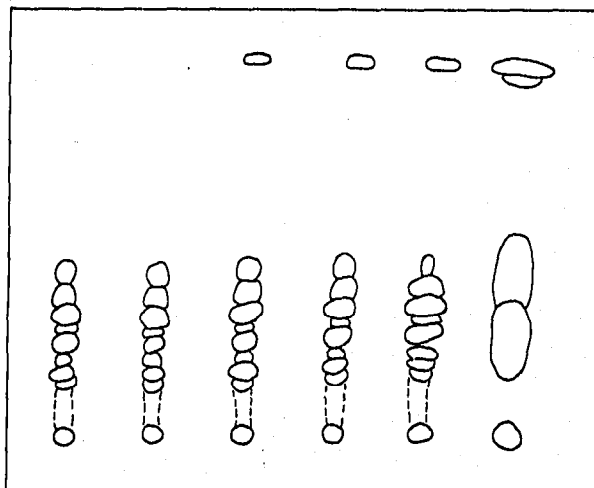
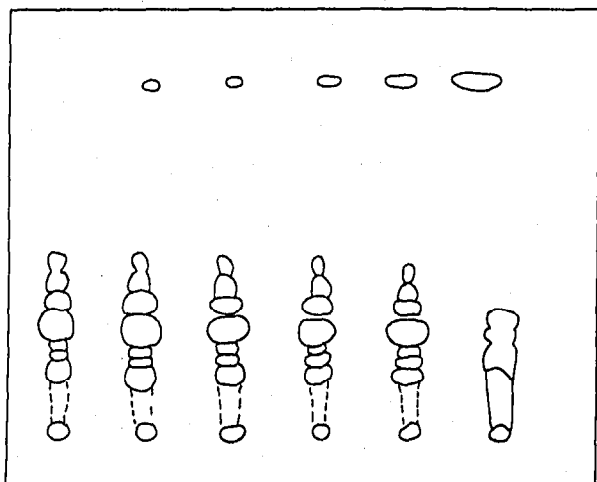


Fig. 1. Thin-layer chromatogram of creosote and creosote containing petroleum diluent. Activated Silica Gel H plate. Solvent: *n*-hexane. Indicator:  $\alpha$ -cyclodextrin followed by iodine fumes. Left to right: creosote alone; creosote containing 0.25, 0.5, 1, and 2% diluent; and diluent alone. 50 mg of each sample diluted with 1 ml of toluene for spotting. 5  $\mu$ l spotted in each case. Diluent: high aromatic heavy fuel oil.

Fig. 2. Thin-layer chromatogram of creosote and creosote containing petroleum diluent. Activated Silica Gel H plate. Solvent: *n*-hexane. Indicator:  $\alpha$ -cyclodextrin followed by iodine fumes. Left to right: creosote alone; creosote containing 0.25, 0.5, 1, and 2% diluent; and diluent alone. 50 mg of each sample diluted with 1 ml of toluene for spotting. 5  $\mu$ l spotted in each case. Diluent: high aromatic distillation pentachlorophenol carrier.

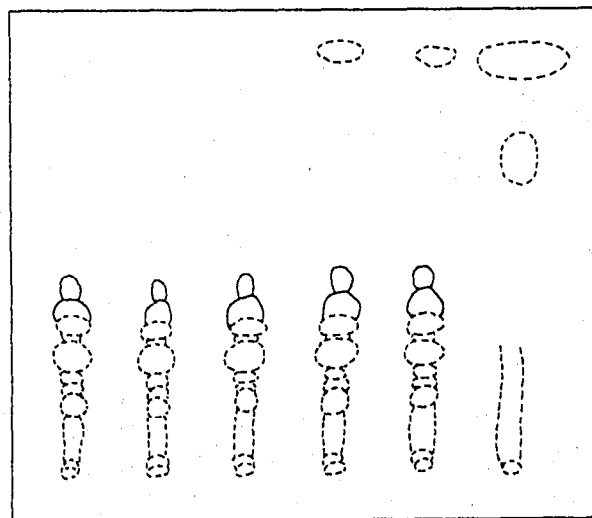
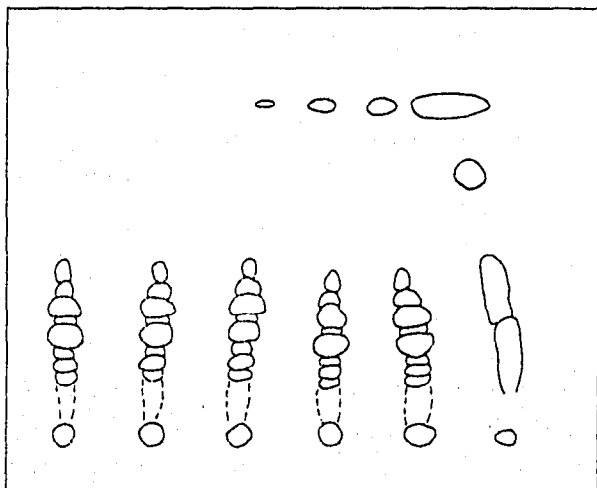


Fig. 3. Thin-layer chromatogram of creosote and creosote containing petroleum diluent. Activated Silica Gel H plate. Solvent: *n*-hexane. Indicator:  $\alpha$ -cyclodextrin followed by iodine fumes. Left to right: creosote alone; creosote containing 0.25, 0.5, 1, and 2% diluent; and diluent alone. 50 mg of each sample diluted with 1 ml of toluene for spotting. 5  $\mu$ l spotted in each case. Diluent: P-9 type heavy pentachlorophenol carrier; high aromatic.

Fig. 4. Thin-layer chromatogram of creosote and creosote containing petroleum diluent. Activated Silica Gel H plate. Solvent: *n*-hexane. Indicator:  $\alpha$ -cyclodextrin followed by iodine fumes. Left to right: creosote alone; creosote containing 0.25, 0.5, 1, and 2% diluent; and diluent alone. 50 mg of each sample diluted with 1 ml of toluene for spotting. 5  $\mu$ l spotted in each case. Diluent: low-aromatic heavy fuel oil.

## RESULTS AND DISCUSSION

Results are shown in Figs. 1 through 4. Under the conditions used, the petroleum could always be detected at the 1 % level and, in most cases, at the 0.5 or even 0.25 % level. By increasing the sample size, *e.g.*, by using 0.10 g diluted with solvent to 1 ml, the detection limit can be reduced to one-half the above limits.

A number of thin layer coatings and solvent systems were used, but best results were obtained with the system described here. Activation of the plates improved the separation between the aromatic fractions and the straight-chain groups.  $\alpha$ -Cyclodextrin complexes with the hydrocarbons, becomes less reactive, and is not colored by the iodine. The spots containing the hydrocarbons appear as white spots on a light brownish-purple background. This indicator should have application in other situations where aromatic groups and straight-chain hydrocarbons are involved. Apparently all of the blending oils, both high aromatic and paraffinic types, contain enough of the hydrocarbons to make the method useful for the detection of these oils.

The method is simple and requires a small amount of equipment. A complete test requires less than 2 h. It can be adapted for use in the field. For use in treating plants where the types of oil being used are known, known solutions may be prepared for spotting adjacent to the unknowns, and concentrations can be altered to meet particular needs of the plant.

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