APPLICATION OF THIN-LAYER CHROMATOGRAPHY TO HYDROCARBON-TYPE ANALYSIS

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SUMMARY

Thin-layer chromatography has been applied to the hydrocarbon-type separation of heavy oils, with emphasis on separation of petroleum resins. A three-stage discontinuous layer-gradient plate was employed and found to give better separation of hydrocarbon types than a single adsorbent plate. Various solvent combinations were utilized and placed in an eluotropic series as applied to petroleum resin separation. Semi-quantitative information was obtained from a completed chromatogram plate by measuring the size of the bands or spots with a ruler or photoelectric scanner.

INTRODUCTION

Many petroleum processing studies require analyses of heavy oil samples in terms of hydrocarbon types. Hydrocarbon-type separations can be carried out by conventional liquid–solid elution chromatography. Resins can be removed by adsorption on an activated clay, and components in the deresined oil can be separated with a column containing both alumina and silica gel. In general terms, the goal is to separate the oil sample into saturates, monoaromatics, polyaromatics, and resins fractions. Conventional chromatographic separation is quite time consuming, and a simpler and faster method is needed to make the technique more widely applicable. Thin-layer chromatographic (TLC) separations can generally be carried out in 20–30 min, and if the developed zones could then be measured rapidly, a considerable advantage would be realized. Several techniques for separating heavy oils by TLC and the measurement of the developed plates have been investigated and are described below.

EXPERIMENTAL

Single adsorbent plates

Single adsorbent plates were prepared using TLC adsorbents with binder and spread in 250-μ layers with a Research Specialties Company variable thickness spreader. The plates were activated in an oven at 105° for 40 min. A rectangular glass

jar was used as a developing chamber. In addition, Eastman Chromagram Sheets, Type K 301-R2 (silica gel without fluorescent indicator) were used. These plates were heated in an oven just before use and developed in a sandwich-type apparatus. The ascending elution technique was used in all cases.

Three-stage plates

CRUMP[1] has reported that the calcium sulfate binder used in conventional silica or alumina thin-layer plates interferes with aromatic hydrocarbon separation and, for this reason, employed a "loose-layer" technique (thin adsorbent layer spread loosely on a glass plate without binder). However, the loose-layer technique is rather difficult to carry out experimentally since any slight jar will disturb the adsorbent bed. For greater handling ease, an investigation of a multi-stage TLC technique with binders was begun in this laboratory. A multi-stage TLC plate is composed of several different adsorbents (three in this case) placed side by side on a single glass plate. This three-stage technique permits the simulation of the larger scale multi-adsorbent separation.

Multi-stage or gradient-layer TLC was suggested by STAHL in 1964[2,3]. He designed special spreaders to prepare gradients of various configurations or several side-by-side layers. BERGER *et al.*[4] separated mixtures of iodide and iodinated derivatives of tetrachlorofluorescein on plates composed of side-by-side layers of silver chloride and a Dowex ion-exchange resin. A simple gradient spreading device that can be applied to the Shandon spreader was reported by WARREN[5]. OULLETTE AND BALCIUS[6] used mixtures of cellulose and Silica Gel G to separate iodine-containing compounds. For our work, a Research Specialties Company Model 200-11 spreader was adapted for three-stage plates by a very simple device, namely two aluminum dividers cut to fit snugly inside the spreader. A bevel or knife edge was placed on the bottom of the dividers. The three-stage plates were prepared using 250-μ layers of Silica Gel G, Aluminum Oxide G, and Florisil G with phosphor.

Spot measurement techniques

The simplest technique for measuring the separated spots or zones is to use a ruler. Measurement with a ruler is facilitated if the plate is marked off in narrow columns (0.3–0.4 cm wide) to confine the developed sample. The separated zones were also measured with two different photoelectric scanner arrangements. The photometer used in both cases was a photomultiplier type that can accommodate several different tube types interchangeably. A long wavelength (3660 Å) UV and a tungsten lamp (15 W, frosted) were used in one arrangement. In addition to these, a short wavelength (2537 Å) UV lamp and 6 W clear tungsten lamp were used in another arrangement.

In the first arrangement, the light source and plate were held fixed and the phototube was moved manually behind the plate. The second scanner system was used principally with strips of Eastman Chromagram Sheet that were pulled across the face of the phototube. The photometer used was an Eldorado Electronics Universal Photomultiplier Photometer Model PH-200, and the photometer signal was fed to a 10 mV Brown recorder. A 1P21 phototube was employed for most of the work. The slit positioned between the TLC strip and the phototube had a width of 0.1 cm and a length of 1.1 cm and was found to give better chromatograms than a

smaller slit that was used initially. The drive motor for the TLC strips was a Gra-Lab timer with the hands removed (speed: 0.5 in./min). A set of cardboard guides and a table were placed over the lower slit so that a strip could be pulled smoothly across the slit. A small hole was placed in the middle of each end of the strips to fasten a small hook for pulling in the forward direction and a counter weight to be fastened to the rear. Amos[7] has used several photoelectric densitometers to measure additive depletion in used lubricating oils and found that precision of $\pm$ 5% could be obtained with the Joyce-Loebl Chromoscan.

RESULTS AND DISCUSSION

Three-stage plates with adjacent layers of silica gel, alumina, and Florisil were used to separate monoaromatic, polyaromatic, and resin cuts from a middle distillate (average molecular weight = 373). The development direction was from the Florisil to the silica gel layer. By the use of mixed developers such as cyclohexane–benzene–ethyl acetate (105 : 1 : 1), it was possible to obtain a developed plate containing one of the separated cuts in each stage. With a mixed developer composed of petroleum ether–ethyl acetate–acetone (380 : 1 : 1), separation was obtained between n-hexadecane and an alkylbenzene in the silica gel stage.

For qualitative comparison, several resin fractions removed from different oil samples were chromatographed on three-stage plates. These fractions were obtained from molecular distillation of West Texas straight run residues having average molecular weights 249, 373, and 959. From the developed chromatograms, it was observed, as expected, that resins from the 249 molecular weight fraction contain less heavy material than the other resins from this series. Resins from the 959 molecular weight fraction cover the largest area on the plate. Two other resin cuts, raw catalytically cracked heavy gas oil (CCHGO) and hydrotreated flashed distillate, formed long streaks from the Florisil up into the alumina, whereas most of the other chromatographed resins formed separated spots in the Florisil and alumina layers. Fig. 1 shows a sketch of the separation obtained with some of these resins.

To determine if three-stage TLC plates offer a definite advantage over plates with one adsorbent alone, a comparison was made of the separated cuts from the 373 molecular weight fraction (1, monoaromatics; 2, polyaromatics; 3, resins) on a three-stage plate and on plates of Alumina G, Silica Gel G, and Florisil G alone. The developer used in all three cases was cyclohexane–benzene–ethyl acetate (42 : 1 : 1). For this investigation, the plates were not sectioned off in columns.

The three-stage plate gave reasonable separation of all three cuts from the 373 molecular weight fraction. Alumina G did not give separation of the mono- and polyaromatics, but the resins remained near the starting point, except for the usual portion that moves with the polyaromatics. Silica Gel G very nearly gave separation of the mono- and polyaromatics, but considerable overlap occurred with the polyaromatics and resins. A Florisil plate gave a fair separation of the three types, but long tails were observed, both with the polyaromatics and resins. The separations obtained in these cases are illustrated in Fig. 2, 3, 4, and 5.

Somewhat different results were obtained when cyclohexane alone was used as developer. On Alumina G, the separation with cyclohexane was slightly better than with the mixed solvent above, but still not equal to that of the three-stage plate. In
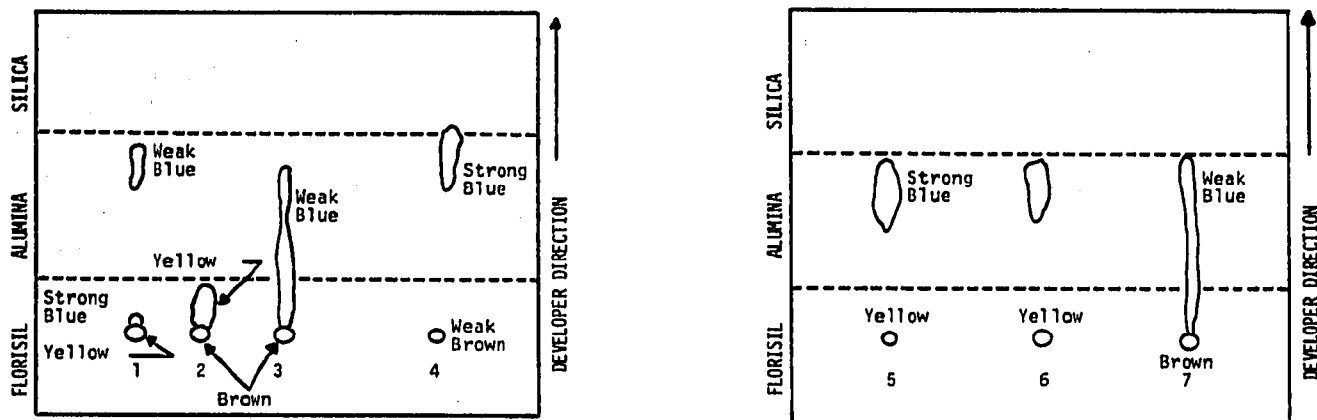
Fig. 1. Three-stage TLC of resin cuts. Developer: cyclohexane–benzene–ethyl acetate (105 : 1 : 1, v/v/v). (1) 249 molecular weight fraction; (2) 373 molecular weight fraction; (3) 959 molecular weight fraction; (4) hydrotreated flashed distillate; (5) hydrotreated CCHGO; (6) hydrotreated CCHGO; (7) hydrotreated flashed distillate.
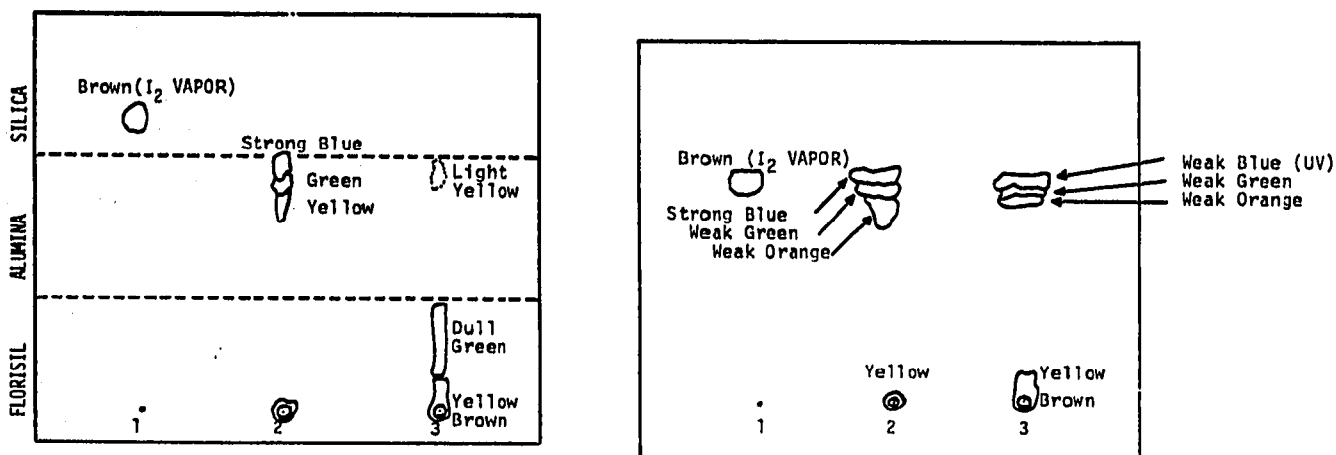

Fig. 2. Comparison of TLC adsorbents—three stage. Developer: cyclohexane–benzene–ethyl acetate (42 : 1 : 1, v/v/v). (1) monoaromatics; (2) polyaromatics, (3) resins.

Fig. 3. Comparison of TLC adsorbents—Alumina G. Developer: cyclohexane–benzene–ethyl acetate (42 : 1 : 1, v/v/v). (1) monoaromatics; (2) polyaromatics; (3) resins.

the silica gel case, cyclohexane development was worse than with the mixed solvent. Development of the Florisil plate with cyclohexane alone gave good separation of the monoaromatics, but the polyaromatics and resins remained near the starting point.

It is apparent from the separations illustrated in Fig. 1 through 5 that not only are the polyaromatic fractions at least partially resolved on the TLC plates (presumably according to molecular polarity) but also the resin fractions can be separated into sub-classes in rather striking fashion in some cases.

Correlation of sample weight and zone length

If different amounts of the same resin sample are developed with cyclohexane on a plate of Florisil alone, a relatively linear calibration curve can be obtained that
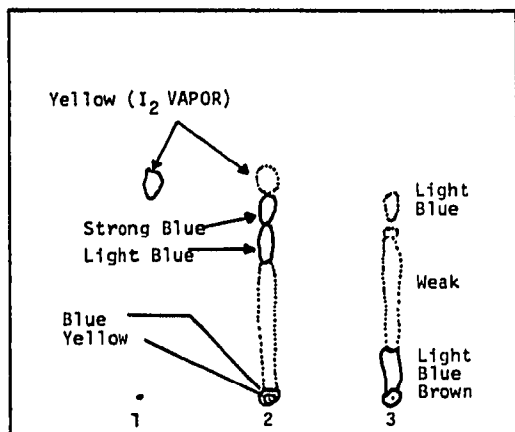
Fig. 4. Comparison of TLC adsorbents—Florisil G. Developer: cyclohexane–benzene–ethyl acetate (42 : 1 : 1, v/v/v). (1) monoaromatics; (2) polyaromatics; (3) resins.
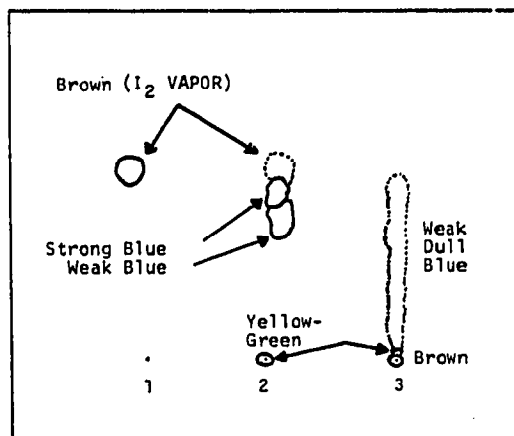
Fig. 5. Comparison of TLC adsorbents—Silica Gel G. Developer: cyclohexane–benzene–ethyl acetate (42 : 1 : 1, v/v/v). (1) monoaromatics; (2) polyaromatics; (3) resins.

TABLE I

EFFECT OF SAMPLE WEIGHT ON ZONE LENGTH

Sample wt. (μg)	Developed distance (cm)	
	Run 1	Run 2
50	3.30	3.10
186	4.65	4.75
304	6.20	6.40
444	7.85	7.70

relates weight of applied sample to length of fluorescent zone. Shown in Table I is a comparison of the zone lengths obtained from duplicate chromatograms of a given resin fraction previously separated from a deasphalted oil with a molecular weight of 772. These samples were developed with cyclohexane for a distance of 15 cm on 500-μ thick plates of Florisil.

The resin content of a sample of heavy flasher tops was determined several times by large-scale liquid–solid chromatography, giving an average value of 6.6 wt. %. This sample was separated with a petroleum ether–ethyl acetate (280 : 1) developer on a three-stage TLC plate marked off in 0.4-cm columns. Based on the length of the fluorescent resin spot in the Florisil layer compared to the total sample length, the results of several analyses are given in Table II. It is obvious from the data in Table II that some uncertainty exists in the result; however, some scatter also occurs in the large-scale liquid–solid chromatographic technique. In one series of large-scale separations, the resin content of repeat runs on a Kuwait flashed distillate varied from 5 to 9%.

Further tests were made with a series of synthetic gas oils prepared from raw CCHGO components. A resin fraction and a deresined oil fraction, separated previously from a CCHGO sample, were recombined to give gas oil samples of about 2, 4, 6, and 10 wt. % resins. The results for resin determinations on these samples are

TABLE II

RESINS IN HEAVY FLASHER TOPS

Run	% resins
1 through 10	4.6, 7.4, 7.7, 7.4 7.1, 7.2, 6.5, 5.4, 5.9, 6.3
Average	6.6

given in Table III. Runs 2 and 3 were duplicates developed on the same plate. Run 5 was different from the others in that samples were diluted so that about the same weight of resin was applied to all spots. After development, the measured lengths were multiplied by the proper factors to account for dilution. This observation suggests that sample size is important and that too large a sample size leads to low results.

TABLE III

RESINS OBSERVED IN SYNTHETIC GAS OIL

Run	Developer	Nominal wt. % resin			
		2	4	6	10
1	Cyclohexane–benzene–ethyl acetate (105 : 1 : 1)	4.6	4.8	—	—
2	Isooctane	2.4	3.8	4.9	6.6
3	Isooctane	2.4	4.1	5.6	7.0
4	Isooctane	2.4	3.9	5.4	7.4
5[a]	Cyclohexane–benzene–ethyl acetate (105 : 1 : 1) Benzene–cyclohexane (40 : 1)	2.0	4.0	6.0	9.6

[a] Developed with two solvent combinations in sequence; first development to 18 cm, second to 4 cm.

Eluotropic series of solvents for resins

When heavy oil samples are separated by TLC into the various component fractions (*e.g.*, via cyclohexane–benzene–ethyl acetate (105 : 1 : 1)), the resin fraction is compact and usually extends over only a relatively small area of the plate near the starting point even though the other component types develop suitably. To avoid some of the problems associated with compacted areas, a number of developer combinations has been examined for their ability to spread the resin fraction over a larger area of the plate. Ideally, all of the other fractions present would be oriented with the new developer in the upper portion of the plate, *i.e.*, either in the silica or alumina stages for the case of a three-stage plate, much as they were with cyclohexane–benzene–ethyl acetate. When only migration of the resin portion of a sample on a three-stage plate was considered, the classification shown in Table IV for various solvents was obtained. A high rating in the eluotropic series does not necessarily mean that a particular solvent combination is eminently suited for development of the resins in a multi-component application. An example is the development of the re-
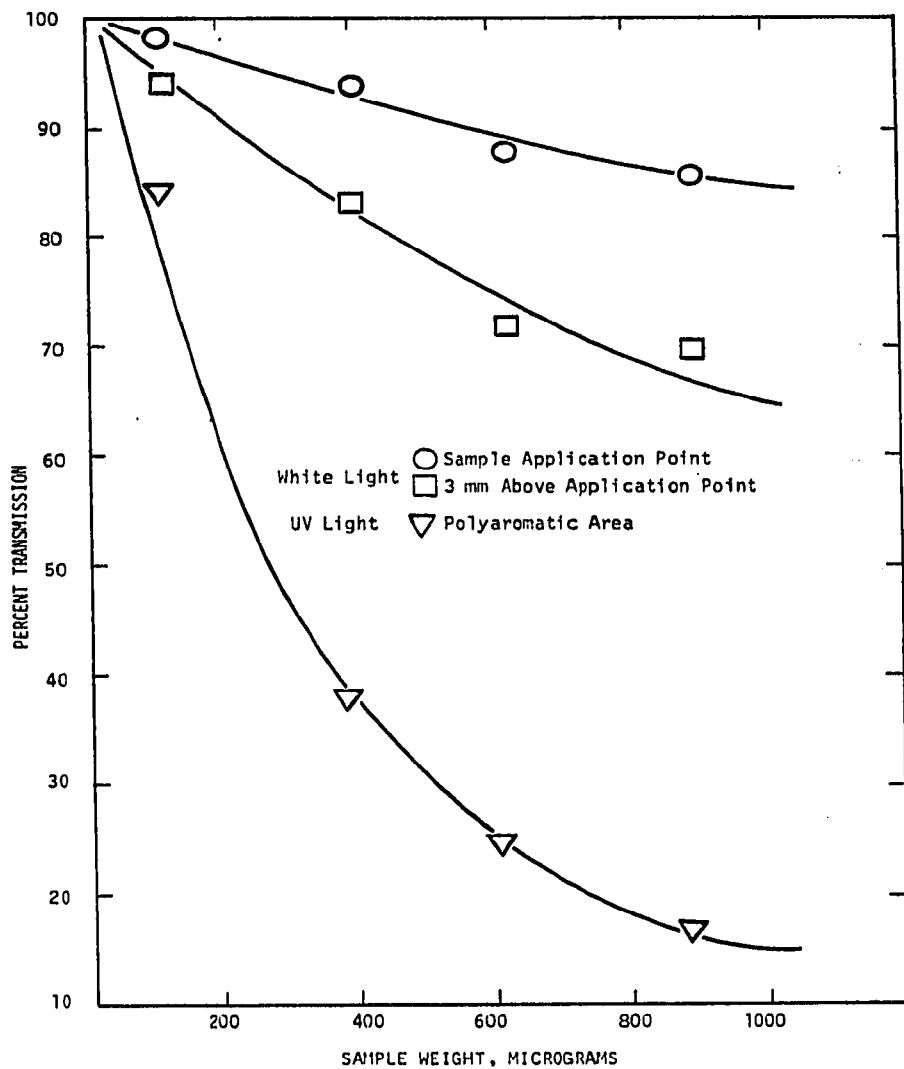
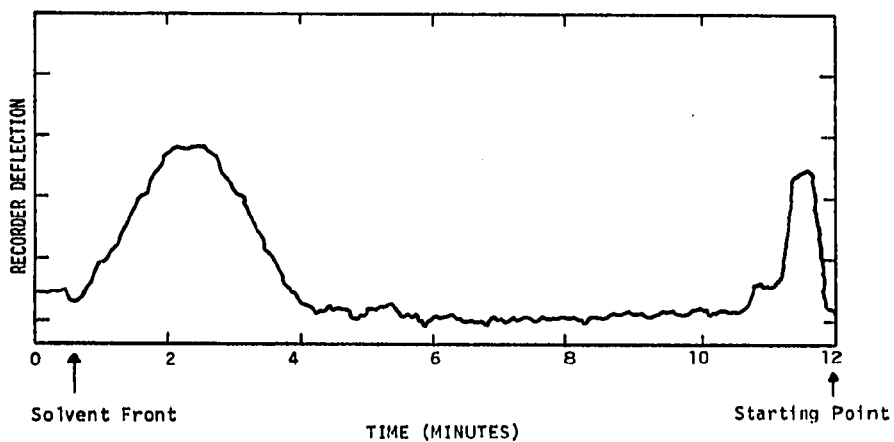Fig. 6. Effect of sample weight on photometer readings.

Fig. 7. Thin-layer chromatogram of hydrotreated flashed distillate.

TABLE IV

ELUOTROPIC SERIES OF SOLVENTS FOR RESINS

Increasing elutive power—
——Water
——Benzene–petroleum ether (4 : 6)
——Methylene dichloride
——Chloroform–petroleum ether (6 : 4)
——Methanol
——Acetone
——Benzene–acetone (1 : 1)
——Benzene–ethyl acetate–dimethyl sulfoxide (10 : 10 : 1)
——Benzene–ethyl acetate (1 : 1)

spective monoaromatic, polyaromatic, and resin cuts from the 373 molecular weight fraction with a solvent mixture composed of 10 : 10 : 1 benzene–ethyl acetate–dimethyl sulfoxide (DMSO). This solvent retarded the monoaromatics relative to the polyaromatics and resins. With a solvent of methanol–DMSO–benzene–ethyl acetate (16 : 3 : 1 : 1), the polyaromatics and monoaromatics were both retarded relative to the resins. Alteration of the elutive power of benzene with cyclohexane, at a ratio of 19 : 1 for example, will approach the desired development of resins from the 373 molecular weight fraction relative to the other cuts.

Photoelectric scanners

    Different amounts of a deasphalted oil sample were developed with cyclohexane on a three-stage plate and scanned by the manual technique. Fig. 6 shows the data obtained from measurements made at three levels on this plate; namely, at the sample application point, at 3 mm above the sample application point, and in the polyaromatic area (alumina) about 10 cm above the starting point. The results obtained are reasonably consistent and suggest the possibility that, with good repeatability of zone development, a photometer with fixed apertures might be used to provide quantitative data.

    The technique of marking off a plate in narrow columns was attempted with Eastman Chromagram Silica Gel Sheets, but the results were not as good as those obtained with the laboratory-prepared glass plates. The principal reason for this difference is that the layer on the Chromagram sheet is somewhat brittle, which results in a ragged edge. The ragged edge permits sample to "leak" out of the column, thus adding to the measuring difficulty.

    Better results were obtained with Chromagram sheets by first developing samples on an 8 × 8-in. sheet and then cutting developed sample strips with scissors. The second scanner arrangement was adapted with guides over the slit so that these small strips could be pulled across the slit with the timer motor. Since much of the resin material is colored, a tungsten lamp was used for most of the work. A recorded chromatogram that was developed with cyclohexane–benzene–ethyl acetate (105 : 1 : 1) is shown in Fig. 7. This strip (silica gel) was scanned from the solvent front to the starting point. The large peak near the solvent front represents the less polar compounds and the peak near the starting point is due to strongly adsorbed polar materials. This was a sample blended in the laboratory to contain 2 wt. % resins and 98 wt. % deresined oil. Preliminary results indicate that over a limited concentration

range, the resin peak height is proportional to concentration and perhaps can be employed for the rapid quantitative measurement of resin content of oils.

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