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IDENTIFICATION OF DYE CARRIER CHEMICALS BY THIN-LAYER CHROMATOGRAPHY

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SUMMARY

A thin-layer chromatography technique is described for the analysis of 14 dye carrier chemicals. Silica gel layers conditioned between 50 and 70% relative humidity are developed with hexane-diethyl ether (98:2). Ultraviolet light, antimony pentachloride or iodine vapor are used for detection. The method represents a simple investigative and quality control method that could be adopted by textile plants and chemical suppliers.

INTRODUCTION

In the textile industry, considerable quantities of various types of chemicals are needed to assist in many manufacturing processes such as bleaching, dyeing and finishing. With the development of permanent press treatments in the early 1960's along with the popularity of knit garments in the 1970's, the use of polyester fibers in these fabrics grew tremendously. As a consequence, significant quantities of dye carrier chemicals, which are used as an auxiliary in the dyeing of polyester, were consumed. It has been estimated that in the United States alone, 40 million kilograms of carrier chemicals are consumed annually.

Dye carriers are used in the dyeing of polyester to help obtain certain general requirements such as color yield, level dyeing and improved fastness properties and decreased dyeing time. When attempts are made to analyze dye carriers, the techniques normally used are gas chromatography and infrared analysis. However, the equipment needed for these analyses is not normally found in most textile plants. Therefore, it would be highly desirable to develop an analytical method based on thin-layer chromatography (TLC), since it would result in a valuable investigative and quality control method that could be easily adopted by textile plants and chemical suppliers. Some early attempts to analyze dye carriers have been reported^{1,2}, but this work was superficial in nature. Recent publications by Perry and Shah³ and Perry and Landers⁴ reported the development of a simple TLC technique to analyze common dye carrier chemicals and now this work has been refined and expanded to include additional carrier chemicals.

The identification is based on the comparison of R_F values of standard solutions of pure carrier chemicals with that of the unknown carrier. In addition, specific visualizing agents are used to help to determine the location of the carrier chemical on the plate and aid in the identification of carriers with close R_F values.

The identification of fourteen carrier chemicals will be discussed.

EXPERIMENTAL

Apparatus

20 × 20 × 0.4 cm glass plates and an S-chamber were used (Camag, New Berlin, Wisc., U.S.A.).

Compounds

Standard solutions of individual carrier chemicals as well as selective mixtures of carrier chemicals were prepared using chloroform as a solvent. The carrier types and concentrations used are listed in Table I.

TABLE I

CONCENTRATION OF CARRIER CHEMICALS USED TO PREPARE STANDARD MIXTURES IN CHLOROFORM

Numbers in parentheses refer to Eastman-Kodak Chemical Catalog 47.

<i>Carrier chemical</i>	<i>Concentration (%, w/v)</i>
<i>Mixture No. 1</i>	
<i>o</i> -Phenyl phenol (2219)	1.0
Butyl benzoate (348)	2.0
Biphenyl (721)	0.2
1-Methyl naphthalene (2415)	1.0
1,2,4-Trichlorobenzene (1641)	20.0
<i>Mixture No. 2</i>	
Dimethyl phthalate (318)	2.0
Dimethyl terephthalate (6580)	2.0
Benzyl benzoate (290)	2.0
Methyl salicylate (466)	4.0
Methyl biphenyl*	0.2
<i>Mixture No. 3</i>	
<i>p</i> -Phenyl phenol (2174)	0.1
Methyl <i>p</i> -toluate/benzoate**	1.0
Methyl benzoate (317)	2.0
Phenyl ether (104)	1.0

* From Dow Chemical, industrial sample.

** From Eastman-Kodak, industrial sample.

Procedure

A 300- μ m layer of Silica Gel DSF-5 (Camag) was applied to the glass plates using a spreader and allowed to dry at 20° for at least 15 h at various controlled humidities. Ten microliters of the unknown carrier as received (usually an aqueous

emulsion) as well as 10- μ l samples of the three mixtures of standard carrier chemicals were spotted 1.5 cm from the base of the plate. Individual standard solutions (10 μ l) may also be spotted as reference samples as needed. The plates were developed in an unsaturated S-chamber to a height of 15 cm using hexane (J. T. Baker, Phillipsburg, N.J., U.S.A.; No. 3-9309) and diethyl ether (Baker; No. 2-9244) as the eluent. When the solvent front had reached the 15-cm interruption line, the plate was allowed to equilibrate for 10 min and then removed from the chamber and allowed to air dry for 5 min.

Detection

Ultraviolet (UV) light (254 and 366 nm) was used for detection as well as general and specific visualizing reagents.

RESULTS AND DISCUSSION

Generally, slightly higher concentrations of the standard carrier chemicals are more effective when using visualizing reagents for detection as compared with UV light. For best results, especially if trichlorobenzene is present, the drying time of the plate should not exceed 10 min since evaporation and/or diffusion of the spots might occur leading to possible problems in detecting the carrier chemicals.

Excellent separation of mixtures of selective dye carriers is obtained even when as many as nine carriers are used in a standard solution.

However, it is best to prepare standard mixtures not containing more than five components. Most commercial products contain no more than three carrier chemicals and, in most cases, usually one or possibly two components are normally used.

Effect of relative humidity

The parameter that had the greatest effect on R_F values was humidity. A series of experiments were conducted to study the effect of relative humidity by allowing the freshly prepared silica gel plates to equilibrate in an atmosphere of controlled relative humidity and temperature. After coating the plates with adsorbent, the plates were allowed to equilibrate at 20° for 15 h at the following relative humidities: 10, 20, 30, 43, 58, 66, 74 and 90%. The conditioned plates were spotted with a mixture of five carrier chemicals (*o*-phenylphenol, butyl benzoate, biphenyl, methylnaphthalene, trichlorobenzene) representing a wide range of R_F values and then developed in the S-chamber. With these particular carriers as well as with other carriers discussed in this paper, the best separation occurs over a humidity range of 50–70%.

In general, humidities over 70% caused many of the carrier chemicals to ascend to the interruption line and humidities of less than 50% do not lead to good separation (Fig. 1).

R_F values for a series of dye carriers obtained at 58% relative humidity and 20° are reported in Table II. A prior publication³ where relative humidity was not closely controlled listed somewhat different R_F values for some of these carrier chemicals, however, if the relative humidity is controlled, excellent reproducibility of R_F values can be obtained. A variation of ± 0.01 in R_F values were obtained in this study.

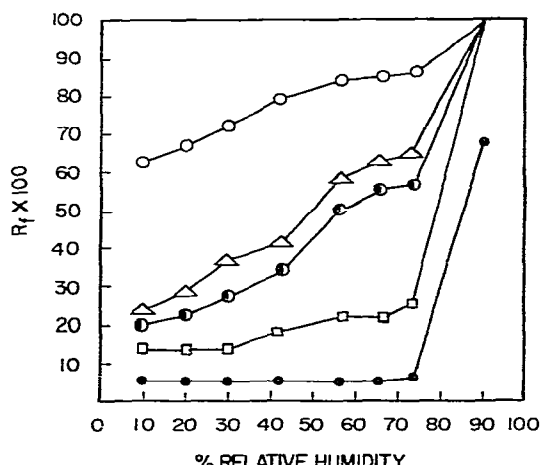


Fig. 1. Effect of relative humidity on R_F values of various carrier chemicals. ●, *o*-Phenylphenol; □, butyl benzoate; ●, biphenyl; △, methylnaphthalene; ○, trichlorobenzene.

TABLE II

R_F VALUES FOR VARIOUS CARRIER CHEMICALS

Run at 58% relative humidity and 20° using hexane–diethyl ether (98:2, v/v) and a silica gel layer (300 μ m) developed to 15 cm.

No.	Carrier chemical	$R_F \times 100$
1	1,2,4-Trichlorobenzene	84.0
2	1-Methyl naphthalene	59.0
3	Biphenyl	50.0
4	Methyl biphenyl	50.0
5	Phenyl ether	39.0
6	Methyl salicylate	27.0
7	Butyl benzoate	26.0
8	Methyl benzoate	25.0
9	Benzyl benzoate	21.0
10	Methyl <i>p</i> -toluate/benzoate	19.0
11	<i>o</i> -Phenyl phenol	6.0
12	Dimethyl terephthalate	5.3
13	Dimethyl phthalate	2.3
14	<i>p</i> -Phenyl phenol	2.0

Effect of hexane source

Three different sources of hexane [J. T. Baker, No. 9309; Mallinckrodt (St. Louis, Mo., U.S.A.), No. 5189; Matheson, Coleman & Bell (East Rutherford, N.J., U.S.A.), No. HX299] as well as *n*-hexane (Fisher Scientific, Pittsburgh, Pa., U.S.A.; No. H-301) were studied to determine the effect of the development solvent upon R_F values. The R_F values varied little among the three sources of hexanes and when chromatograms were run with *n*-hexane, sharper spots, better separation but slightly lower R_F values were obtained. However, for practical purposes, hexane is satisfactory to analyze dye carrier chemicals.

Visualizing reagents

Since dye carrier chemicals are colorless, the use of visualizing reagents was investigated in a hope to find chromogenic reagents which would be specific to certain carriers in order to supplement R_F data.

One of the most informative visualizing reagents found was antimony pentachloride (No. 18205; Applied Science Labs., State College, Pa., U.S.A.), which gave a wide range of colors with many of the dye carriers. Fig. 2 is a drawing of a development of 14 carrier chemicals and the colors formed when a plate was lightly sprayed with a 20% solution of antimony pentachloride in chloroform and heated for 10 min at 150°. Most of the colors formed were fairly stable and were easily seen on a white background. When the sprayed plate was exposed to iodine vapors after the heat treatment, several carriers which were not made visible with antimony pentachloride spray appeared as white spots. Some dulling of the colored spots occurred but this did not seriously affect the results.

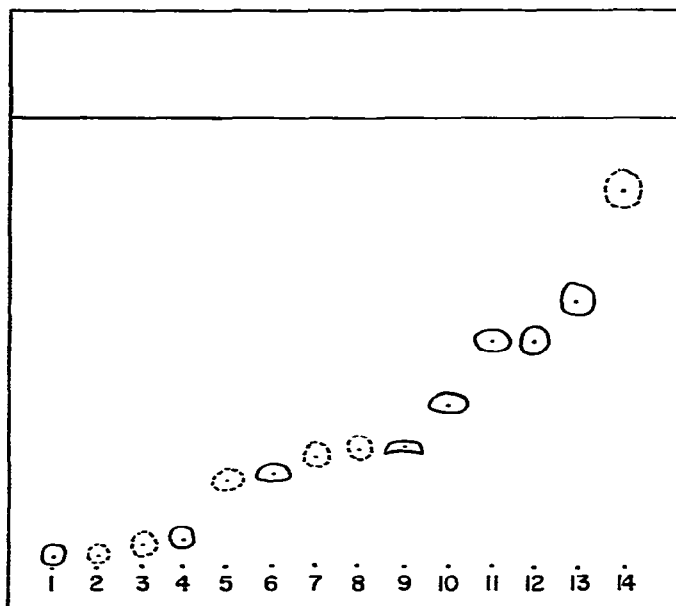


Fig. 2. A typical development with hexane-diethyl ether (98:2, v/v) of 14 carrier chemicals visualized with antimony pentachloride. Spots: (N.V. = no visualization) 1 = *p*-phenyl phenol; (light brown) 2 = dimethyl phthalate (N.V.); 3 = dimethyl terephthalate (N.V.); 4 = *o*-phenyl phenol (dark brown); 5 = methyl *p*-toluate/benzoate (N.V.); 5 = benzyl benzoate (brown); 7 = methyl benzoate (N.V.); 8 = butyl benzoate (N.V.); 9 = methyl salicylate (yellow); 10 = phenyl ether (red-orange); 11 = methyl biphenyl (purple); 12 = biphenyl (light purple); 13 = 1-methyl naphthalene (grey-green); 14 = 1,2,4-trichlorobenzene (N.V.).

Minimum concentration of carrier chemicals detected by use of UV light and chromogenic reactions are listed in Table III.

A more detailed study was published previously⁴, with a variety of visualizing reagents with many of the dye carriers reported in this paper describing both general and specific location reagents.

TABLE III

MINIMUM CONCENTRATION OF CARRIER CHEMICAL REQUIRED FOR VISUALIZATION WITH VARIOUS TECHNIQUES

N.V.: compound not visible.

No.	Carrier chemical	Antimony pentachloride (μg)	Iodine vapor (μg)	Ultraviolet (μg)
1	1,2,4-Trichlorobenzene	N.V.	100.0	100.0
2	1-Methyl naphthalene	0.6	50.0	1.2
3	Biphenyl	10.0	N.V.	0.06
4	Methyl biphenyl	1.0	N.V.	1.0
5	Phenyl ether	0.3	50.0	2.5
6	Methyl salicylate	50.0	0.3	0.6
7	Butyl benzoate	10.0	100.0	1.2
8	Methyl benzoate	N.V.	100.0	10.2
9	Benzyl benzoate	1.2	10.0	1.2
10	Methyl <i>p</i> -toluate/benzoate	N.V.	N.V.	0.6
11	<i>o</i> -Phenyl phenol	N.V.	100.0	0.3
12	Dimethyl terephthalate	0.6	0.07	0.3
13	Dimethyl phthalate	N.V.	100.0	2.5
14	<i>p</i> -Phenyl phenol	5.0	0.06	0.06

When unknown commercial dye carriers were analyzed using the developed TLC technique, excellent results were obtained. In addition, the emulsification system which is needed to prepare aqueous emulsions for the practical use of these products, did not interfere with the analyses.

Further studies are under way using this technique to determine the amount of dye carrier adsorbed by polyester fiber during dyeing. Also, this technique is being investigated to determine the cause of dye spots in dyeing as a result of precipitation of carrier chemicals on fabric during the dyeing process. Quantitative analyses is also currently being studied using visualizing reagents to help determine the size and intensity of the spots. The techniques currently being used in this area are Purdy and Truter⁵ algebraic spot area method, spot area and density using photographs and minimum spot visibility method.

CONCLUSIONS

A simple, rapid TLC technique which separates and identifies many common dye carrier chemicals used by the textile industry to help dye polyester fiber has been developed. The advantage of an inexpensive simple TLC technique is that most textile plants do not have the expensive infrared and gas chromatography equipment needed to analyze these carrier chemicals. Therefore, textile plants as well as chemical suppliers can now use TLC as a valuable investigative and quality control system.

For best separation, the coated plates should be conditioned between 50 and 70% relative humidity prior to spotting and development. However, a relative humidity of 58% is recommended for conditioning for the optimum reproducibility. The use of antimony pentachloride as a visualizing reagent provides a valuable adjunct to R_F values for the identification of common dye carrier chemicals. Commercial

dye carriers can be readily analyzed using this technique without interference with the emulsification system used in these products. Research currently under investigation indicates that this technique may be useful to analyze the adsorption of carrier chemicals by polyester fiber during dyeing, for analyzing dyeing defects caused by carriers and also as a possible means of understanding dye carrier mechanisms.

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