

CHROM. 11,972

THIN-LAYER CHROMATOGRAPHY OF SLIGHTLY SOLUBLE SUBSTANCES AT ELEVATED TEMPERATURE

GUSTAV SZÉKELY and PETER BAUMGARTNER

Ciba-Geigy AG, CH-4002 Basle (Switzerland)

SUMMARY

As they are virtually insoluble at room temperature, various organic pigments, dyes and intermediates were not amenable to conventional thin-layer chromatography. However, at elevated temperature they dissolved in high-boiling solvents and could be separated on small silica gel plates maintained at *ca.* 150°.

INTRODUCTION

Thin-layer chromatographic (TLC) separations are usually performed at ambient temperature, and work at elevated temperature only rarely has been described. Stahl^{1,2} developed a thermostated chamber suitable for temperatures up to about 50° and investigated the dependence of the separation on temperature. Turina and co-workers^{3,4} also heated the plates to *ca.* 50° in a hot-plate chromatographic method. The volatile eluent evaporated during the separation process, which resulted in focusing of the zones and a lower detection limit for trace components.

Using a lithium nitrate and potassium nitrate eutectic at 270°, Druding⁵ separated inorganic cations on silica gel layers.

The present work shows that slightly soluble organic substances can be investigated by TLC if one uses suitable high-boiling solvents at temperatures around 150°.

EXPERIMENTAL

A 5-ml volume of a high-boiling solvent was added to 5 mg of finely powdered sample in a test-tube, which was then heated in a dry block heater with temperature control. The solvents used were N-methyl-2-pyrrolidone, quinoline, 1-bromonaphthalene and nitrobenzene. Many substances that are virtually insoluble at ambient temperature could be dissolved in one of these solvents or their mixtures at 150° at a concentration of 0.1% or more.

The application of the sample solutions to the plates and the chromatographic development were also carried out at the same temperature. Usually 2-5 μ l of the hot sample solution were applied by means of calibrated capillaries. Small 10 \times 10 cm plates obtained by cutting conventional 20 \times 20 cm silica gel pre-coated plates were

used⁶. Accessories intended for use with the EVA-chrom applicator, *i.e.*, the capillary holder and the capillary dispenser (W+W Electronic, Münchenstein, Switzerland), proved suitable for manipulating the hot capillaries. On a thermostated hot-plate the TLC plate, the capillary dispenser and the calibrated capillaries were pre-heated to the required temperature, the hot capillary was picked up with the holder and filled with the hot sample solution, which was then applied on the starting point of the TLC plate. By means of tweezers, the plate was then placed in a prepared developing tank (twin-trough chamber for use with 10 × 10 cm plates; Camag, Muttenz, Switzerland). The chamber had been filled in advance with 5 or 10 ml of solvent, on one or both sides, and pre-heated to the required temperature in an oven placed in a ventilated fume cupboard. The ventilation chimney of the oven was attached directly to the main ventilation system in order to ensure a slight negative pressure. After development for 10–15 min to a separation distance of 7 cm, the plates were removed, cooled and evaluated, usually under daylight and UV light.

Evidence for artifacts

The question of whether the observed chromatographic zones really represented substances present in the original sample or rather substances that had formed by oxidation and/or pyrolysis was tested by re-chromatography of the main zone. For this purpose use was made of the dry-transfer technique of Székely⁷: the main zone was scraped off and the powder obtained was placed on a 3 × 3 mm area at the start of a fresh TLC plate from which the layer had previously been removed (Fig. 1). The powder was compressed with a spatula. If in the second run under the same chromatographic conditions the transferred zone migrated as a single zone, it could be assumed that the secondary zones of the first run had not been formed by decomposition of the main zone. The presence of secondary zones in the second run, however, would indicate that the main sample constituent had decomposed under the given conditions. This might be suppressed either by using a slightly lower operating temperature or by choosing a different solvent.

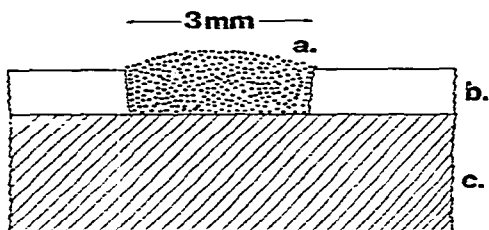


Fig. 1. Schematic representation of the dry transfer. (a) Transferred zone; (b) silica gel layer; (c) glass plate.

RESULTS

Twenty-two high-boiling organic solvents were used as eluents, including hydrocarbons, halogenated hydrocarbons and esters. The selection criteria were high boiling point, good thermal stability, low price and varied polarity. Using the selected solvents, indigo was chromatographed as a test substance on silica gel layer at 150° and the elutropic series shown in Table I was obtained.

TABLE I
ELUOTROPIC SERIES OF HIGH-BOILING SOLVENTS

Solvent	R_F for indigo	Solvent	R_F for indigo
1-Chloro- <i>n</i> -dodecane	0.06	Di- <i>n</i> -propyl phthalate	0.73
1-Bromonaphthalene	0.12	Di- <i>n</i> -butyl adipate	0.75
1-Chloronaphthalene	0.15	Diethyl phthalate	0.81
2-Ethyl-naphthalene	0.16	Dimethyl phthalate	0.84
1-Methylnaphthalene	0.32	<i>n</i> -Butyl benzoate	0.95
Diphenyl ether	0.32	Ethyl anthranilate	0.97
Diisooctyl adipate	0.43	Nitrobenzene	1.00
Diisobutyl phthalate	0.58	2-Methylbenzothiazole	1.00
Benzyl benzoate	0.58	N-Methyl-2-pyrrolidone	1.00
Di- <i>n</i> -butyl phthalate	0.63	2-Ethyl- <i>n</i> -hexanol	1.00
Benzophenone	0.70	Quinoline	1.00

In a second series of experiments we also investigated two- and multi-component eluents. Good separations could be achieved with two-component mixtures with a polar and a non-polar constituent, such as 1-methylnaphthalene-N-methyl-2-pyrrolidone or di-*n*-butyl phthalate-nitrobenzene.

Finally, the method was tested with many practical examples, a few of which are as follows:

(a) Indigo was chromatographed on silica gel at 150° with di-*n*-butyl phthalate-N-methyl-2-pyrrolidone (9:1). A reddish secondary zone was observed, which probably corresponds to the *cis*-isomer of indigo (Fig. 2).

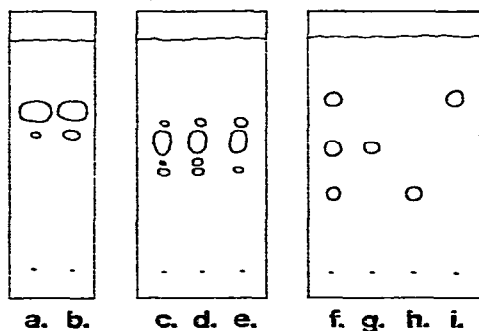


Fig. 2. Separation of indigo at 150°. (a) and (b) two different samples. Layer: silica gel 60 F₂₅₄ (Merck) pre-coated plate. Solvent: di-*n*-butyl phthalate-N-methylpyrrolidone (9:1). Application: 5 μl each of 0.1% sample solutions in bromonaphthalene. Separation time: ca. 15 min for a 7-cm separation distance.

Fig. 3. Separation of an intermediate for the vat dye Cibanonrot 4B separated at 160°. (c), (d) and (e) three different laboratory samples. Layer: silica gel 60 F₂₅₄ (Merck) pre-coated plate. Solvent: benzyl benzoate-nitrobenzene (1:1). Application: 5 μl each of 0.1% sample solutions in 1-methylnaphthalene. Separation time: ca. 10 min for a 7-cm separation distance.

Fig. 4. Identification of the pigments in a polyvinylidene chloride (PVCD) foil. Separation temperature: 140°. (f) 5 μl of a 5% PVDC solution in 1-bromonaphthalene-nitrobenzene (1:1); (g) Chromophthalgelb GR; (h) Chromophthalscharlach R; (i) Chromophthalorange 4R. Layer: silica gel 60 F₂₅₄ (Merck) pre-coated plate. Solvent: 1-methylnaphthalene-nitrobenzene (3:2). Separation time ca. 10 min for a 7-cm separation distance.

(b) An intermediate for the vat dye Cibanonrot 4B (a derivative of triazinylaminoanthraquinone), separated at 160° on silica gel with benzyl benzoate-nitrobenzene (1:1), showed a number of secondary zones (Fig. 3).

(c) Three pigments contained in an orange plastic foil were identified by their colours and R_f values (Fig. 4). The foil, made from polyvinylidene chloride, was first dissolved in a hot mixture of 1-bromonaphthalene-nitrobenzene (1:1) and then chromatographed at 140° on silica gel with 1-methylnaphthalene-nitrobenzene (3:2).

CONCLUSION

The above examples show how substances that are virtually insoluble at room temperature can often be analysed successfully by TLC at elevated temperature. It should be noted, however, that the samples to be analysed must exhibit a sufficient thermal stability.

ACKNOWLEDGEMENTS

The experimental work was carried out by G. Bechdolff and W. Birri, to whom we express our sincere gratitude.

REFERENCES

- 1 E. Stahl, *Chem.-Ing.-Tech.*, 36 (1964) 941.
- 2 E. Stahl, *Dümschicht-Chromatographie*, Springer, Berlin, Heidelberg, New York, 1967, p. 95.
- 3 S. Turina, Z. Šoljić and V. Marjanović, *J. Chromatogr.*, 39 (1969) 81.
- 4 S. Turina and Jamnicki, *Anal. Chem.*, 44 (1972) 1892.
- 5 L. F. Druding, *Anal. Chem.*, 35 (1963) 1744.
- 6 R. Delley and G. Székely, *Chimia*, 32 (1978) 261.
- 7 G. Székely, *J. Chromatogr.*, 42 (1969) 543.