Correlation of retention parameters of pesticides in normal- and reversed-phase systems and their utilization for the separation of a mixture of 14 triazines and urea herbicides by means of two-dimensional thin-layer chromatography

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Abstract

The selectivities of TLC systems were compared by use of correlations between $R_{F(II)}$ and $R_{F(I)}$ (by analogy with two-dimensional TLC). The greatest spread of points, indicative of individual selectivity, was obtained for nonaqueous mobile phases on silica and aqueous mobile phases on octadecyl silica adsorbent wettable with water (RP-18 W). The correlation of R_F values in normal- and reversed-phase systems was utilized in the practical separation of a mixture of 14 triazines and urea herbicides using two-dimensional thin-layer chromatography on a Multi-K CS5 dual phase (3 cm strip of octadecyl silica parallel to silica layer). The plate was videoscanned showing the real picture of the plate. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Thin-layer chromatography (TLC) is one of four important chromatographic techniques (besides GC, HPLC and supercritical fluid chromatography); its main advantages are low cost and the possibility of analyzing a large number of samples (e.g. 40) simultaneously. TLC analysis of pesticides is especially suitable at sites where the concentrations of pesticides might be high (e.g. in the chemical industry, and the transport, storage, and distribution

of pesticides, and liquidation of dumping grounds of toxic substances).

The objective of analysis is as a rule identification of pesticides, possibly the determination of composition of pesticide mixtures and quantitative analysis. The obvious choice of adsorbent for TLC is silica as the most popular, selective and inexpensive material. Relationships between R_F values and mobile phase composition have been determined for almost 100 moderately polar pesticides in systems of the type silica (and some of them also on thin layers of other adsorbents, e.g. alumina, Florisil, CN, NH$_2$, DIOL), nonpolar or weakly polar diluent (heptane or chloroform)+polar modifier (ethyl acetate, tetrahydrofuran, dioxane, diisopropyl ether, or acetone) [1–4]. These relationships constitute a retention database

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[4]. The database of retention (R_F) vs. eluent composition plots of pesticides can be utilized in several ways:

(i) for planning effective two-dimensional TLC separations of complex mixtures of pesticides on Multi-K SC5 dual phase, combined with videoscanning [5];

(ii) the database enabled to choose optimal conditions for preparative column separation into weakly polar, moderately polar and polar fractions [6];

(iii) and for application of TLC as a pilot technique for HPLC [7] and transferring retention data from TLC to HPLC.

The selectivity of a chromatographic system is the main parameter which decides about the success of separation in chromatography, both on an analytical and preparative scale. For a pair of compounds the

Fig. 1. The pesticides investigated in TLC and 2D-TLC.

selectivity is quantitatively characterised by the separation coefficient ($\alpha = k_{II}/k_I$ for substances II and I); for a larger group of compounds the R_{FII} vs. R_{FI} (or R_{MII} vs. R_{MI}) correlations provide general selectivity characteristics [8].

Two-dimensional thin-layer chromatography (2D-TLC) is an effective method for the separation of larger groups of substances. The theory and practical applications of this method were studied by Guiochon et al. [9–11] and computer simulation of 2D-TLC systems was described by Nurok et al. [12,13]. The advantages of 2D-TLC have been pointed out by Poole [14]. Nyiredy [15,16] described the technique of joining two different adsorbent layers on a single carrier plate; precoated two-adsorbent plates with a narrow zone of SiO_2 and a wide zone of RP 18 (or vice versa) are commercially available from Whatman (Multi-K SC5 and CS5 plates).

The largest differences are obtained by combination of normal-phase (NP) system of the type silica/nonaqueous eluent and reversed-phase system (RP) of the type octadecyl silica/water + methanol (e.g. Refs. [17–20]).

Pesticides have been occasionally analysed by 2D-TLC method, e.g. *N*-nitroso-triazine herbicide (cyanazine and terbuthylazine and their reaction products) using different mobile phases for each dimension on silica gel plates [21]. A computer-assisted, statistical scanning method was reported by Wang for optimizing separation of a mixture of eight pesticides by 2D-TLC [22].

2. Experimental

Test pesticides 1–14 listed in Fig. 1 were purchased from the Institute of Organic Industry (IPO, Warsaw, Poland).

Dioxane, *n*-hexane, acetonitrile, methanol and tetrahydrofuran were pro chromatography grade from Merck (E. Merck, Darmstadt, Germany); ethyl acetate was analytical reagent grade from Polish Reagents (POCh, Gliwice, Poland).

TLC experiments were performed on 10 cm×20 cm glass-backed precoated silica gel HPTLC 60 F_{254} plates (E. Merck; No. 1.05729) and on 10 cm×10 cm glass-backed precoated octadecyl silica gel HPTLC RP-18 W F_{254S} (No. 1.13124.0001).

The pesticides were spotted as 0.5% solutions and HPTLC plates were developed to a distance of 9 cm in horizontal, PTFE DS chambers (Chromdes, Lublin, Poland) [23]. The spots were detected either under UV illumination at $\lambda = 254$ nm or in iodine vapours. All experiments were repeated three times.

2D-TLC was performed on 20 cm×20 cm glass-backed dual phase Multi-K CS5 (3 cm zone of octadecyl silica gel parallel to silica layer), purchased from Whatman (Maidstone, UK).

The mixture of pesticides was spotted pointwise on the line of start (at distances of 1 cm from the edges of the plate) on the narrow (3 cm) zone of octadecyl silica gel on Multi-K CS5 plate. The plate was developed in the first dimension (step A) using a reversed-phase eluent of methanol–water (60:40, v/v) on the narrow zone of octadecyl silica gel (which was on the left side during step A). After drying in air for 12 h, the plate was turned by 90° (so that the
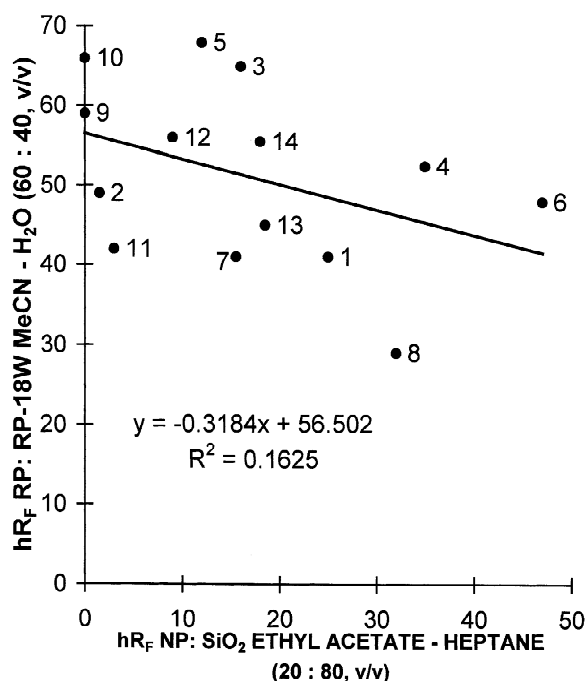

Fig. 2. Correlation hR_F vs. hR_F for 2D-TLC system: NP, ethyl acetate–*n*-heptane (20:80, v/v) on silica gel and RP, acetonitrile–water (60:40, v/v) on octadecyl silica adsorbent wettable with water (RP-18 W); the numbering and abbreviations are as given in Fig. 1. The quality of 2D-TLC chromatogram is inversely proportional to R^2 given in the diagram.

narrow zone of octadecyl silica gel was on the start of the next step). The Multi-K CS5 plate was developed in the second dimension (step B) using a normal phase eluent of tetrahydrofuran–*n*-heptane (20:80, v/v) on the wide zone of silica adsorbent.

The spots were detected under UV illumination at $\lambda = 254$ nm.

In addition, a videoscan was made showing a real picture of the Multi-K CS5 plate with complete separation of the 14-component mixture of herbicides (Videoscanner Hitachi 3 CCD; videoscan was registered with programme Videostore 2).

3. Results and discussion

In the first series of experiments the relationships between R_F values and mobile phase composition have been determined for 14 herbicides in normal-phase system of the type silica/*n*-heptane + polar modifier (ethyl acetate, AcOEt; tetrahydrofuran, THF and dioxane, Dx).

In the second series of experiments relationships between R_F values and mobile phase composition
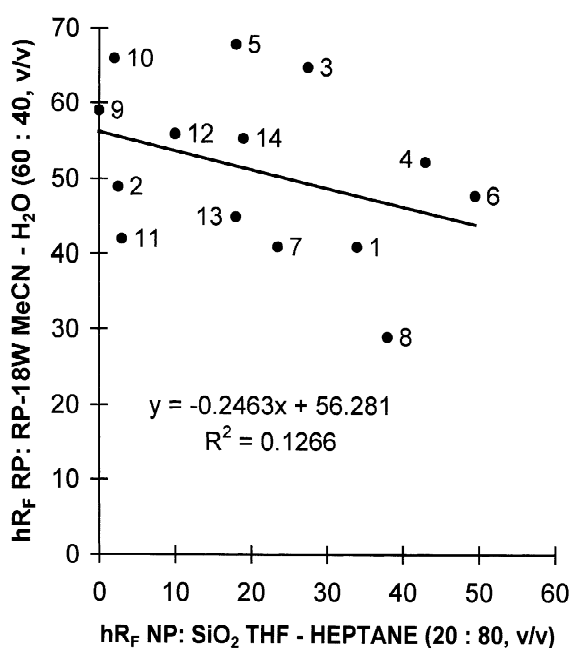
have been determined for these pesticides in a reversed-phase system of the type octadecyl silica/water + polar modifier (acetonitrile, MeCN; methanol, MeOH and tetrahydrofuran, THF).

On the basis of the results obtained it is possible to choose the best pairs of selective systems (normal- and reversed-phases) for the separation of the mixture of 14 herbicides. The group selectivity was compared applying the correlation of R_F coefficients, in analogy to 2D-TLC (Figs. 2–7).

The selectivity was differentiated for the individual modifiers. The selectivity of pesticides for correlation of normal-phase and reversed-phase is good in water–acetonitrile systems (Figs. 2–4), better in water–methanol systems (Figs. 5–7). For correlation of normal-phase and water–tetrahydrofuran systems the selectivity for most of the pesticides is markedly worse (Fig. 8).

The greatest spread of points (Fig. 5–7), indicative of individual selectivity, was obtained for
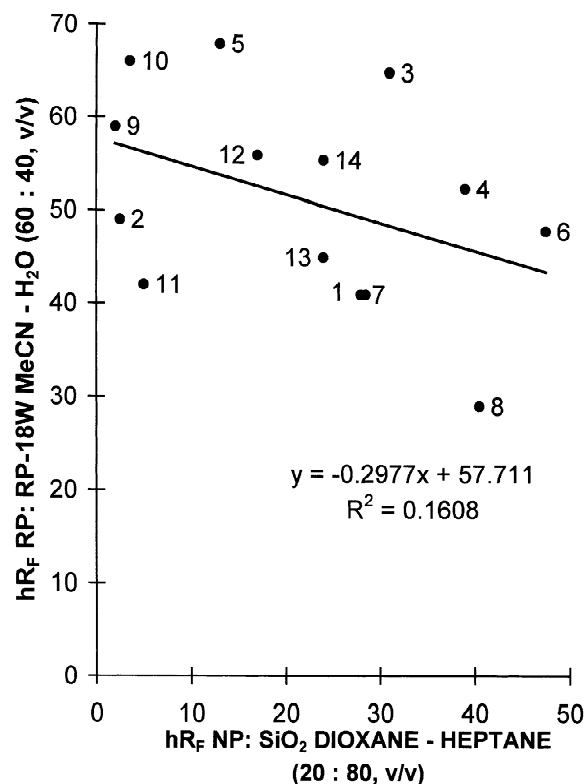

Fig. 3. As in Fig. 2; NP, tetrahydrofuran–*n*-heptane (20:80, v/v); RP, acetonitrile–water (60:40, v/v).

Fig. 4. As in Fig. 2; NP, dioxane–*n*-heptane (20:80, v/v); RP, acetonitrile–water (60:40, v/v).
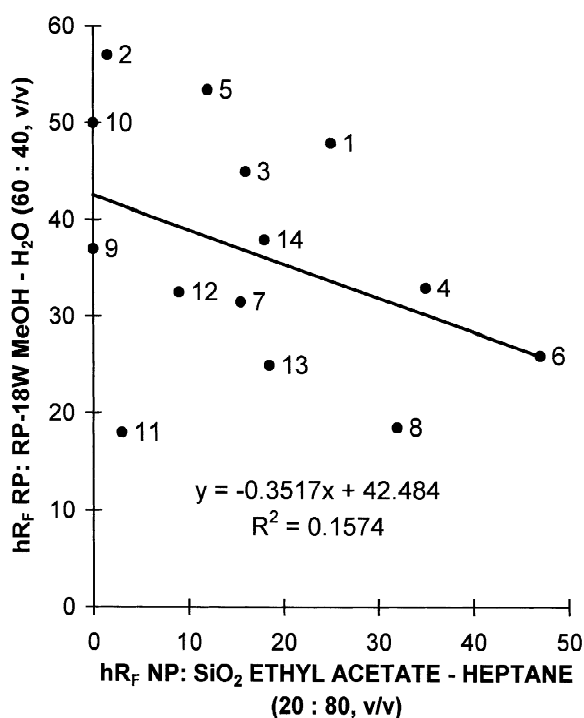
Fig. 5. As in Fig. 2; NP, ethyl acetate–n-heptane (20:80, v/v); RP, methanol–water (60:40, v/v).
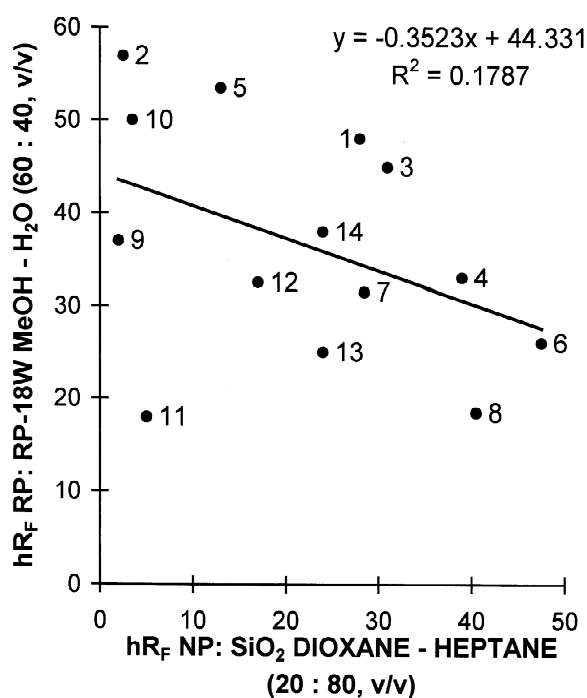

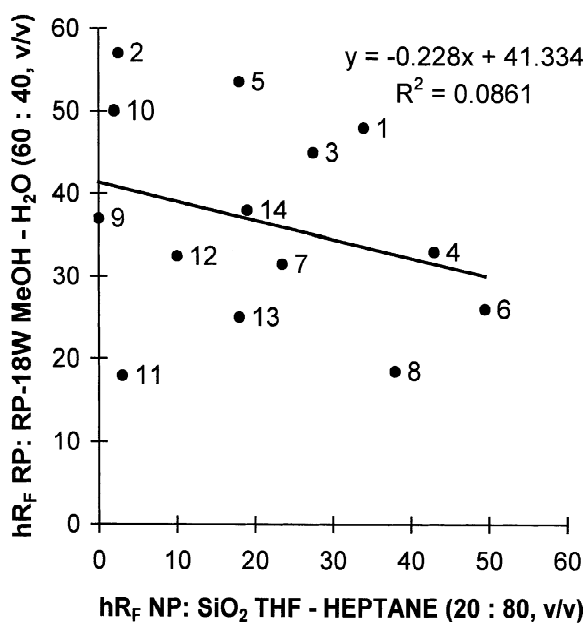Fig. 7. As in Fig. 2; NP, dioxane–n-heptane (20:80, v/v); RP, methanol–water (60:40, v/v).

Fig. 6. As in Fig. 2; NP, tetrahydrofuran–n-heptane (20:80, v/v); RP, methanol–water (60:40, v/v). This pair of NP/RP systems was chosen for 2D-TLC.

nonaqueous mobile phases on silica and aqueous mobile phases of methanol–water (60:40, v/v) on octadecyl silica adsorbent wettable with water (RP-18 W). The optimal (lowest) correlation of normal- and reversed-phase systems (Fig. 6) was observed for the mixture of 14 triazine and urea herbicides using two-dimensional thin-layer chromatography on Multi-K CS5 dual phase (3 cm strip of octadecyl silica gel on silica layer). In addition, a videoscan showing the real picture of the plate was made (Fig. 9), which shows complete separation of the complex mixture of pesticides.

4. Conclusion

The retention database and correlations of retention coefficients was used for correct identification and complete separation of a mixture of 14 herbicides with 2D-TLC and videoscanning, which would not be possible for single developments in the RP and NP systems. The optimal eluent composi-
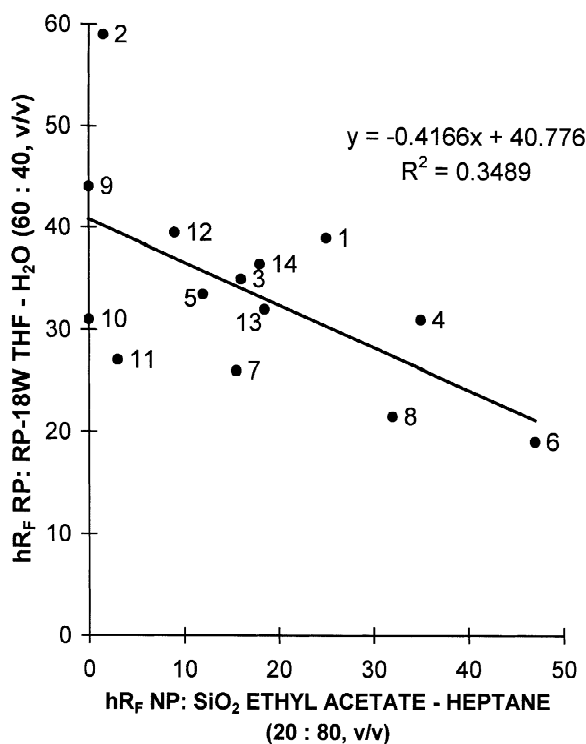
Fig. 8. As in Fig. 2; NP, ethyl acetate–n-heptane (20:80, v/v); RP, tetrahydrofuran–water (60:40, v/v).

Fig. 9. Videoscan of the Multi-K CS5 plate which shows complete separation of the 14-component mixture of pesticides for 2D-TLC system: RP, methanol–water (60:40, v/v) on octadecyl silica adsorbent (step A) and NP, tetrahydrofuran–n-heptane (20:80, v/v) on silica gel (step B); numbers as in Fig. 1.

tions for NP and RP one-dimensional systems were chosen from R_F vs. eluent composition plots for the widest ranges of R_F values of the components.

Although silica and octadecyl silica adsorbents from different producers were used for hR_F vs. hR_F correlation (Fig. 6) and in the 2D-TLC experiment (Fig. 9), the two figures are quite similar.

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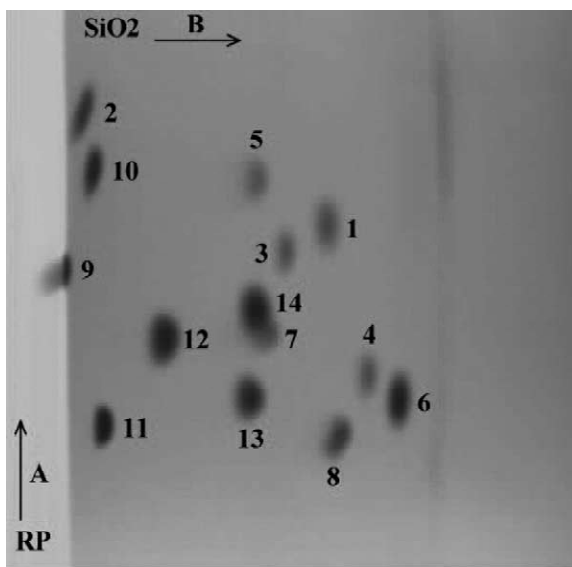[17] E. Soczewiński, M.A. Hawryl, A. Hawryl, Chromatographia 54 (2001) 789.

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