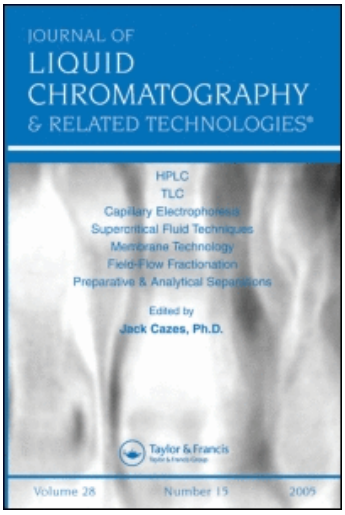


**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Effect of Overdevelopment on the TLC Separation of Three 2,6-Dinitro 4-/Trifluoromethyl/-Aniline Derivatives

T. Cserháti[a]; L. Gyõrfi[b]
[a] Plant Protection Institute of Hungarian Academy of Sciences, Budapest, Hungary [b] Ministry of Agriculture and Food Plant Protection and Agrochemical Centre,

**To cite this Article** Cserháti, T. and Gyõrfi, L.(1990) 'Effect of Overdevelopment on the TLC Separation of Three 2,6-Dinitro 4-/Trifluoromethyl/-Aniline Derivatives', Journal of Liquid Chromatography & Related Technologies, 13: 10, 2013 — 2020
**To link to this Article: DOI:** 10.1080/01483919008049009
**URL:** http://dx.doi.org/10.1080/01483919008049009

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(10), 2013-2020 (1990)

# EFFECT OF OVERDEVELOPMENT ON THE TLC SEPARATION OF THREE 2,6-DINITRO-4-/TRIFLUOROMETHYL/-ANILINE DERIVATIVES

T. CSERHÁTI[1] AND L. GYÕRFI[2]
[1]*Plant Protection Institute of Hungarian Academy of Sciences*
*Herman 0.15*
*1022 Budapest, Hungary*
[2]*Ministry of Agriculture and Food*
*Plant Protection and Agrochemical Centre*



## ABSTRACT

N-ethyl-N-/2-methyl-2-propenyl/, N-butyl-N-ethyl and N,N-dipropyl derivatives of 2,6-dinitro-4-/trifluoromethyl/ /-aniline were separated on alumina TLC layers with n-hexane eluent applying one, two and three developments. The second development enhanced considerably the resolution and also the detection limit. The third development had a negligible effect on the resolution, however the detection limit was further increased. Due to the lateral diffusion the half width of peaks decreased linearly with the number of developments. The data proved that the third development had no additional advantage the optimal separation was achieved by two developments.

## INTRODUCTION

The herbicides Ethalfluralin = N-ethyl-N-/2-methyl-2-propenyl/-2,6-dinitro-4-/trifluoromethyl/aniline /1/; Benfluralin = N-ethyl-N-butyl-2,6-dinitro-4-/trifluo-

romethyl/aniline /2/ and Trifluralin = N,N-dipropyl-2,6-dinitro-4-/trifluoromethyl/aniline /3/ have been extensively applied in up-to-date agrochemical practice. Their residues have been determined by GLC with ECD /4,5,6,7/. It was established that Trifluralin and Benfluralin interfered with the determination of Ethalfluralin on 5% XE-60 GC column, however Ethalfluralin was sufficiently separated on a 120 cm 5% Carbovax 20M column from the other two herbicides. According to our knowledge the simultaneous separation of the three herbicides has never been achieved by GLC with packed columns /8/. Appropriate separation was carried out only by means of capillary columns /9/.

As the more and more strict regulations of environmental pollution and food quality require the exact determination of pesticide residues the separation of these three herbicides is of great importance.

In order to improve separation the technique of overdevelopment has been successfully applied more than twenty years ago in thin-layer chromatography /10,11/, however ,the advantages and disadvantages of this technique have never been evaluated by adequate mathematical-statistical methods.

The objectives of our work were to separate these three herbicides by thin-layer chromatography and to evaluate the effect of overdevelopment on the resolution and on the detection limit.

## MATERIAL AND METHODS

Herbicides Benfluralin, Ethalfluralin and Trifluralin were purchased from Eli Lilly and Co, USA and applied without further purification. DC-Plastikfolien Alumi-

**niumoxid 6o F254 neutral /Type E/ /Merck,FRG/ plates were activated at 14o $^{o}$C for an hour before development.** The n-hexane was of analytical grade.Herbicides were dissolved in n-hexane in the concentration range 2,5-o,o5 mg per $cm^3$; 1 $mm^3$ of each solution was plotted on the plates.The plates were developed by n-hexane in sandwich chamber and then dried at room temperature. The second and third developments were carried out in identical manner.After each development the spots were evaluated by a Shimadzu Dual-Wavelength TLC Scanner CS-93o at 39o nm wavelength.The integration limit was set to 5.ooo area unit.The separation efficiency of developments was characterized by the resolution Rs /12/.

In order to establish the effect of developments on the detection limit linear correlations were calculated between the quantity of herbicide on the spot and the spot area for each development:

$$\mu g \text{ herbicide} = a + b.\text{spot area}$$

To determine the theoretical limit of detection the herbicide quantity / μg / corresponding to 5.ooo area unit was calculated. To evaluate the influence of the number of developments on the half width of peak linear correlation was calculated betwen the half width of peak and the number of developments:

$$\text{peak half width} = a + b.\text{number of developments}$$

## RESULTS AND DISCUSSION

A typical chromatogram is shown in Fig.1. Oppositely to GLC the critical step is the separation of Ethalfluralin and Benfluralin which is unadequate after the first development. The second development increased considerably the separation but the third separation step did

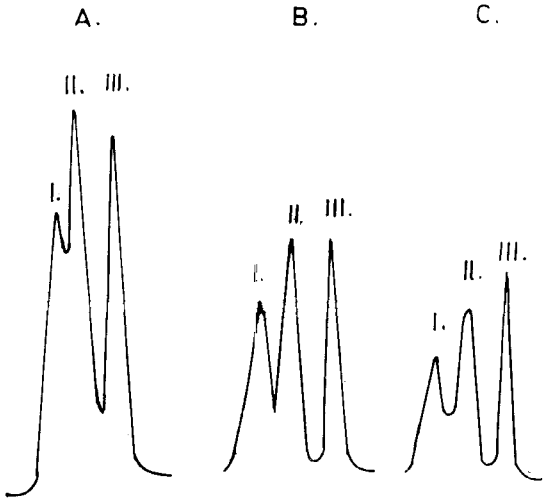


FIGURE 1. Effect of the number of developments on the separation of Ethalfluralin /I/, Benfluralin /II/ and Trifluralin /III/ after one /A/, two /B/ and three /C/ developments.



not improved it significantly. The average values of resolution /Rs/ support this observation / see Table 1./. The parameters of linear correlations between the quantity of herbicide on the spot and the area measured by the TLC scanner are listed for Trifluralin in Table 2. Highly significant correlations were found betwen the TLC scanner area output and the quantity of Trifluralin on the spot for the first two developments. In these cases the intercept /a/ values which can be considered as systematic error are low. The correlation, however significant, deteriorates at the third development and the intercept value increases. These findings and the results of Table 1. indicate that the third development has no beneficial effect on the separation.

TABLE 1.
Dependence of Resolution /Rs/ of Ethalfluralin /I/ , Benfluralin /II/ and Trifluralin /III/ on the Number of Developments

| No of development | Rs between I - II | I - III | I - III |
|---|---|---|---|
| 1 | o,44 | 1,32 | o,74 |
| 2 | o,66 | 1,86 | 1,34 |
| 3 | o,64 | 2,o4 | 1,42 |

TABLE 2.
Parameters of Linear Correlations Between the Trifluralin Quantity on the Spot /ug/ and the Area Unit of TLC Scanner

| No of development | a | $b.10^5$ | $s_b.10^6$ | significance level % |
|---|---|---|---|---|
| 1 | $-6,35.10^{-4}$ | 2,6o | o,4o | 99,9 |
| 2 | $5,62.10^{-2}$ | 2,73 | 1,99 | 99,9 |
| 3 | $2,28.10^{-1}$ | 2,84 | 3,12 | 98,o |



The calculated detection limits were o,13; o,19 and o,37 µg for the first, second and third developments respectively. This results shows that the second development increases negligibly the detection limit but the third one markedly enhances it. We have to stress that these limits are related to 5.ooo area unit of TLC scanner sensitivity. At lower area units the detection limit is between o,o3 - o,o5 µg herbicide per spot.
No significant differences were observed between the results of Table 2. and the similar results concerning Ethalfluralin and Benfluralin therefore these data are not included.
The effect of developments on the peak heigth and width is visualized in Fig.2. Due to the lateral diffusion the peak heigth decreases and the peak width increases with growing number of developments. The correlations between the peak half width and the number of develop-

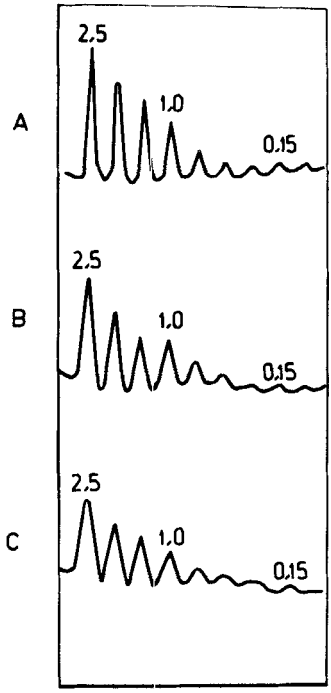


**FIGURE 2. Effect of the number of developments on the peak heigth and width of Trifluralin.Arabic numbers indicate µg Trifluralin per spot. A = after one development; B = after two developments; C = after three developments.**



ments is significantly linear:

peak half width = 1,93 + /o,52 ± o,o4/.development number

$r = o,9583 \qquad r_{99,9\%} = o,76o3$

The finding indicates that the peak half width increases in each development, however this deteriorating effect is counterbalanced in the second development by the growing differences in retention resulting in better separation. In the third development this deteriorating effect inhibits the further improvement of separation.

Summarizing our results we conclude that the separation of herbicides Ethalfluralin, Benfluralin and Trifluralin can be carried out on alumina layers with n-hexane as eluent using two consecutive developments. Due to the growing peak width the third development does not improve the separation and increases the detection limit.

## REFERENCES

1. Skylakis,G., Anastasiadis,B., Buendia,J., Bayo,R. M., Oran,Y. and Waldrep,W.T., El-161 , a new preplant incorporated herbicide for control of grass and dicotyledonous weeds in cotton. In Proc. 12th Br.Weed Control Conf. London,British Crop.Prot. Council, 1974, p.795.

2. Lewis,W.M., Preemergence crabygrass control with comparison of spray and granular applications. In Proc.18th South.Weed Control Conf. Crops Sci.Dep. N.Carolina State Coll., Raleigh, 1965, p.118.

3. Alder,E.F., Wrigth, W.L. and Soper,Q.F., Control of seedling grasses in turf with diphenylacetonitrile and substituted dinitroaniline. In Proc.17th N. Centr.Weed Control Conf. Ed.: Eli Lilly et Co., Greenfield Labs.,Greenfield, Indiana, 196o,p.23.

4. Day,E.W., Anal.Methods Pestic.Plant Growth Regul. X. Zweig,G. and Sherma,J., eds., Academic Press, New York, 1978,p.341.

5. Johnson.W.S. and Frank.F.,Anal.Methods Pestic. Plant Growth Regul.VIII. Zweig,G. and Sherma,J., eds., Academic Press, New York,1976, p.335.

6. Tepe,J.B. and Scroggs,R.E., Anal.Methods Pestic. Plant Growth Regul.V. Zweig,G. and Sherma.J.,eds Academic Press, New York, 1967,p.527.

7. Fehringer,N.V. and Walters,S.T., Evaluation of Capillary Gas Chromatography for Pesticide and Industrial Chemical Residue Analysis.I. Comparison of Retention Ratios Obtained on Methyl Silicone Coated Capillary Columns with Published Values for Packed Columns. JAOAC 67, 91, 1984.

8. Cserháti,T., Dobrovolszky,A.,Fenyvesi,É. and Szejtli, J., Beta-Cyclodextrin Polymer Beads as GC Packings. J.High Res.Chrom.Chrom.Commun. 6, 442, 1983.

9. Deleu,R. and Copin,A., Separation of Pesticides by Capillary Gas Chromatography. Part 3:Dinitroaniline Herbicides. J.High Res.Chrom.Chrom.Commun. 5, 682, 1982.

lo. Brenner,M. and Niederweiser,A., Durchlaufende Dünnschicht Chromatographie. Experientia 17, 237, 1961.

11. Hüttenrauch,R. and Schulze,J., Dünnschichtchromatographische Trennung glykosidischer Antibiotika. Pharmazie 19, 334, 1964.

12. Snyder,L.R. and Kirkland,J.J.,Introduction to Modern Liquid Chromatography, Second Edition, J.Wiley and Sons, New York, 1979, p.34.