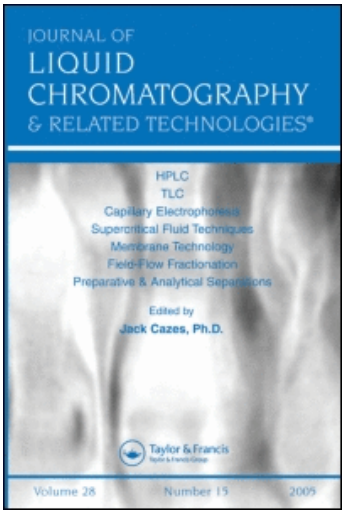

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A RESIDUE TECHNIQUE FOR UREA HERBICIDES USING CATALYTIC HYDROLYSIS ON SILICA GEL PLATES

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ABSTRACT

Urea herbicides are catalytically hydrolyzed to the corresponding aniline. The reaction occurs in situ on silica gel TLC plates making use of the acidic silanol groups. The anilines are then further reacted in situ with dansyl chloride and the fluorescent derivatives separated on the same plate. The sensitivity and selectivity of this technique permit the analysis of urea herbicide residues in soil and water samples with good reproducibility and a minimum of sample clean-up.

INTRODUCTION

Recently, we have compared the merits of thin-layer and high-performance column liquid chromatography for the determination of metoxuron [3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea] and its by-products in commercial formulations[1]. Although

* On transfer of work July 1 1978 - March 1 1979 from the Food Directorate, Health Protection Branch, Ottawa, Canada.
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in these cases detection and quantitation by means of UV-absorption was satisfactory both from the selectivity and sensitivity point of view, this does not apply when residue analysis is considered.

Frequently, residue analysis of phenyl ureas is carried out via a hydrolysis step to form the (substituted) aniline, followed by e.g. gas chromatography[2-4] or quantitative thin-layer chromatography[5], respectively. Unfortunately, for many of these ureas, the hydrolysis step is quite time-consuming and cumbersome; for e.g. metoxuron it will go to completion only after refluxing for 4-6 h[6]. Therefore, in this study we have investigated the use of a simplified hydrolysis procedure - if possible coupled with in situ fluorescence labelling - on (HP)TLC plates, and its potential for residue analysis.

EXPERIMENTAL

Reagents. Linuron (N-methyl-N-methoxy-N'-(3,4-dichloro)-phenyl urea), diuron (N,N-dimethyl-N'-(3,4-dichloro)-phenyl urea), metoxuron (N,N-dimethyl-N'-(3-chloro-4-methoxy)-phenyl urea) and 3-chloro-4-methoxy aniline (OCPA) were obtained as gifts from Sandoz (Basle, Switzerland). A sample of Maloran (N-methyl-N--methoxy-N'-(3-chloro-4-bromo)-phenyl urea) was kindly provided by the customs laboratories (Amsterdam, the Netherlands). 3,4-Dichloroaniline and dansyl chloride (5-dimethylamino-naphthalene--1-sulfonyl chloride) were purchased from Fluka (Buchs, Switzerland) and Merck, respectively. All other reagents were of normal analytical-grade quality.

For the urea herbicides and anilines stock solutions of 1 mg/ml were prepared in dichloromethane.

Procedure and apparatus

Soil sample. 25 g of soil were shaken for 2 h with 120 ml methanol in a 1-l round-bottom flask. After standing over

night, the soil was vacuum-filtrated. This procedure was repeated using 60 instead of 120 ml methanol. Next, the filtrate was diluted with water to 500 ml and extracted 3 times with 50 ml dichloromethane. The combined dichloromethane fractions were evaporated to dryness and the residue dissolved in 5 ml dichloromethane.

Clean-up of the sample solutions[7] was done on a 1-cm diameter column containing 5 g of 2% deactivated 60-100-mesh Florisil (Sigma, St. Louis, Mo., U.S.A.), and having a 1-cm layer of sodium sulphate at the top. After rinsing the column with hexane, the 5-ml sample was placed on the column and eluted with 30 ml of (1) dichloromethane-hexane (30:70), (2) acetone--hexane (15:85) in which fraction linuron elutes, and (3) acetone-hexane (50:50). This third fraction which contains diuron and metoxuron was evaporated to near dryness in a Rotavapor (Büchi, Flawil, Switzerland); the residue was dissolved in 2 ml dichloromethane.

Next, 8 spots (2 for the sample, 2 for the blank and 4 for the standards) of 10 µl each were applied with a 10-µl syringe (Hamilton, Bonaduz, Switzerland) on a 10 × 10 cm^2 silica gel-60 F 254 HPTLC (or TLC) plate (Merck), 10 mm from the bottom, 15 mm from the edge and 10 mm from each other. This plate was covered with a glass plate, heated at 160°C for 25 min and subsequently cooled to room temperature. After this hydrolysis step, all spots - except for one blank - were overspotted with 4 µl of 0.2% dansyl chloride in acetone and the plate covered immediately with the glass plate again. Dansylation, which was carried out in the dark, took 1 h.

The spots were now preconcentrated by developing the plate with acetone over a distance of about 1 cm. Next, the plates were accommodated for 30 min in a 21.5 × 21.5 × 6 cm rectangular tank (Camag, Muttenz, Switzerland), which was saturated with benzene-triethylamine-acetone (75:24:1). Development with this solvent mixture over a distance of about 9 cm took ca. 15 min. After drying with a stream of nitrogen, the spots were scanned

(λ_{ex} = 350 nm, λ_{em} = 518 nm, 10-nm slits) on a Spectrofluorometer MPF 43 A (Perkin Elmer, Norwalk, Conn., U.S.A.) with a TLC attachment and Kipp DB-8 recorder (Kipp, Delft, the Netherlands).

RESULTS AND DISCUSSION

Hydrolysis. According to Voss[3], hydrolysis of metoxuron and other phenyl urea herbicides has to be carried out in 10 M NaOH, about 3 h being required in order to achieve a quantitative reaction. We have shown that under more gentle conditions (1 M NaOH) as described in ref.5, quantitative hydrolysis of metoxuron does not occur, although a 90-min reaction time at 80°C suffices for the complete hydrolysis of linuron and maloran (chlorbromuron). For metoxuron, Wisson et al.[6] have recommended acid hydrolysis (1 N H_3PO_4) for up to 6 h under gentle reflux conditions. In the present study, using normal reflux conditions, a 98 ± 1% S.D. conversion of metoxuron into OCPA was obtained in only 3.5 h.

In order to simplify these techniques and to avoid working with complex glassware and large volumes of aggressive chemicals, it was proposed to carry out the hydrolysis of the phenyl urea herbicides at elevated temperature in the adsorbed state on polar adsorbents such as silica gel. At 90°C, a 15-20% conversion is observed for linuron and maloran in 1 h, while with metoxuron and diuron values of less than 5% are found under the same conditions. Raising the temperature to 110°C ensures an almost complete hydrolysis of linuron and maloran within 40 min; however, after this period of time, about 50% of metoxuron still remains on the plate. At 130°C, quantitative hydrolysis of metoxuron takes some 2 h, after which time diuron has been converted for about 50%. A further increase of temperature to 160°C is required in order to fully hydrolyze diuron and to ensure the rapid hydrolysis (30-45 min) of all four herbicides (see Fig.1). Since the anilines formed decompose at such a high temperature, a 25-min heating time was chosen as optimal with regard to aniline formation versus aniline decomposition.

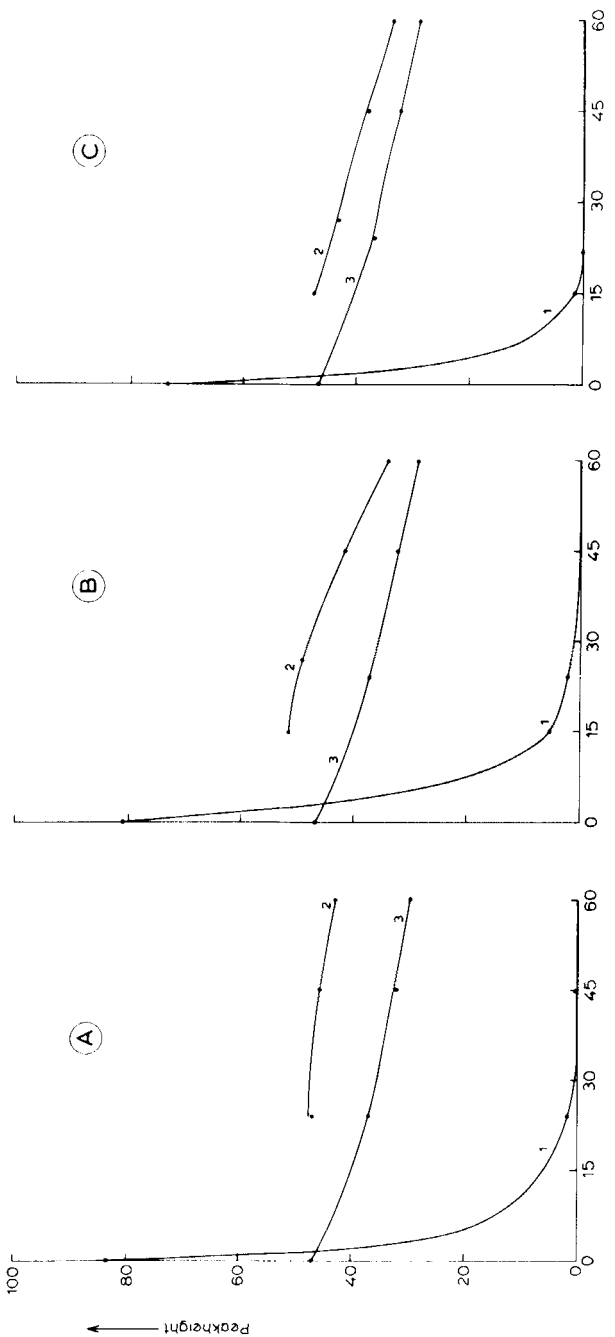

FIGURE I. Hydrolysis curves of A metoxuron, B diuron, and C linuron at 160°C. Line 1 decomposition of the urea herbicide, 2 formation of the aniline, and 3 reference degradation of the aniline.

Under these conditions, yields of 101 ± 2% of OCPA, and 86 ± 6% and 79 ± 2% of 3,4-dichloroaniline were recorded for metoxuron, diuron and linuron, respectively. Here, it should be stressed that covering the silica gel plate with an empty glass plate during the heat treatment is necessary in order to obtain reproducible results. Results of hydrolysis on TLC and HPTLC plates are compared in Table I. The data show good mutual agreement; still, one should prefer the HPTLC technique on account of its higher precision.

Possibly, the accelerated rate of hydrolysis of the herbicides is due to the catalytic action of the slightly acidic silanol groups present on the silica gel surface. A proposed reaction scheme is shown in Fig.2 (cf. refs.8, 9 and 10). It seems important to note that rapid hydrolysis only takes place if heating occurs at or above the melting-point temperature of the various compounds (linuron, 93-94°C; maloran, 94-96°C;

TABLE I

Comparison between the analysis of metoxuron with TLC and HPTLC*

	TLC		HPTLC	
	yield OCPA** in µg	% S.D.	yield OCPA** in µg	% S.D.
4 different plates	5.6		5.6	
	5.2	± 1.6	5.7	± 0.9
	5.3		5.5	
	5.6		5.6	
4 spots on 1 plate	5.6		5.6	
	5.5	± 1.4	5.5	± 0.6
	5.4		5.5	
	5.8		5.5	

* Hydrolysis at 160°C for 20 min.
**Determined after the hydrolysis of 8.6 µg metoxuron/10 µl spot.

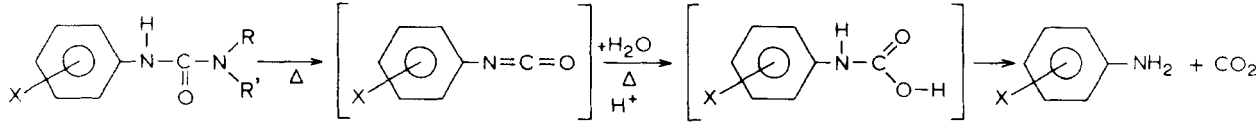

FIGURE II. Proposed reaction scheme for the catalysed hydrolysis of the urea herbicides on silica gel plates.

metoxuron, 128-129°C; diuron, 158-159°C). Lastly, we emphasize that linuron and maloran are easily hydrolysed in batch under such relatively mild conditions as used by Frei et al.[5], whereas metoxuron and diuron are not. In other words, the presence of an N-alkoxy group appears to facilitate the hydrolysis of phenyl urea herbicides.

Dansylation and TLC. The dansylation of the anilines resulting from the hydrolysis step has been described earlier[5]. According to this paper, it is possible to carry out this reaction by overspotting the aniline spots with an acetone solution containing an at least 25-fold excess of dansyl chloride - the large excess of reagent being necessary because of its relatively rapid hydrolysis. Dansylation proceeds quantitatively in about 1 h in the dark.

In the present study, the above method was adapted; since no further sample handling was required, as the next step HPTLC was carried out using benzene-triethylamine-acetone (75:24:1) as mobile phase. The R_F values of the dansylated 3,4-dichloroaniline, OCPA and aniline were 0.01 (0.04), 0.11 (0.16) and 0.29 (0.48), respectively; the values in brackets refer to HPTLC with non-equilibrated plates. It should be noted that the hydrolysed dansyl chloride, which displays an intense blue fluorescence, stays at the point of origin in the selected solvent system and hence does not interfere in the analysis.

For metoxuron, calibration curves - as recorded by means of fluorodensitometry - were linear (R = 0.9993) in the range of 6-520 ng per spot. The stability of the dansylated derivatives of metoxuron as well as the other herbicides was satisfactory for analytical purpose, a 20% reduction in sensitivity occurring in 24 h. The detection limit was calculated to be about 5 ng, which agrees with earlier results[5]. Spraying the thin-layer plate with e.g. a 20% solution of triethanolamine in isopropanol resulted in significantly higher signals. Unfortunately, however, the data so obtained were rather irreproducible; as a consequence, spraying was omitted.

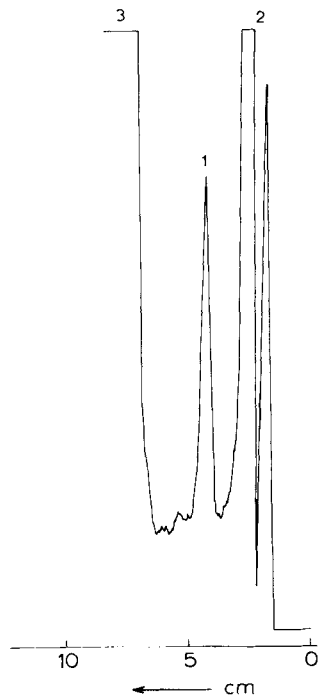

FIGURE III

Fluorescence densitometric scan of a soil sample, spiked with 1 ppm metoxuron 1; 2 is hydrolysed dansyl chloride and 3 the excess dansyl chloride.
Conditions: see Experimental.

Residue analysis. The applicability of the present technique to residue analysis was demonstrated using water and soil samples. With the latter sample (cf. Fig.3), due to its nature (very rich organic soil), an additional clean-up procedure was required, as reported in the experimental section. The recovery for 4 samples each spiked with 1 ppm metoxuron was 65.0 ± 2.5%. The analysis of water samples spiked with 20 ppb metoxuron did not present any difficulties.

CONCLUSION

Compared with older techniques, catalytic hydrolysis of phenyl urea herbicides on silica gel thin-layer plates offers several advantages such as significant time-saving, simplicity of handling, avoidance of the use of aggressive chemicals and excellent reproducibility. The short reaction time prevents losses due to decomposition of the anilines to become excessive.

The present approach no doubt has potential for the analysis of related classes of compounds, such as the N-phenylcarbamates. Besides, since it keeps all operations at a convenient and economic micro-scale, it will also come in useful when coupling in situ hydrolysis with types of reactions other than dansylation. Lastly, the selectivity of the fluorescence labelling coupled with the subsequent chromatographic step permits considerable simplification of the sample pre-clean-up and renders the technique suitable for trace determinations in complex matrices.

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