

## The chromatographic identification of substituted urea herbicides

Although many procedures have been described for the determination of residues of substituted urea herbicides, adequate methods for the identification of residues of these compounds have not been reported. Analytical procedures based on hydrolysis to the aniline derivative such as those of DALTON AND PEASE<sup>1</sup>, KIRKLAND<sup>2</sup>, GUTENMAN AND LISK<sup>3</sup>, WEBLEY AND MCKONE<sup>4</sup> and HENKEL<sup>5</sup> can at best only distinguish between compounds in which the substituents in the aniline ring vary. Thin-layer and paper chromatographic procedures have been proposed by MAJOR<sup>6</sup>, ABBOTT *et al.*<sup>7</sup>, GUTH *et al.*<sup>8</sup>, KATZ AND FASSBENDER<sup>9</sup>, FINOCCHIARO AND BENSON<sup>10</sup> and HENKEL<sup>11</sup> but in each case only a few of the commercially available ureas were considered. The gas chromatographic behaviour of twelve ureas is reported by MCKONE AND HANCE<sup>12</sup> but the resolution under the conditions described was not adequate for identification.

The object of the work described here was to evaluate the TLC behaviour of eleven urea herbicides in a range of solvent systems and to select suitable systems which when used in conjunction with gas chromatography<sup>1,13</sup> would provide a means for the identification and determination of residues of these compounds.

### Materials and methods

Thin-layer plates (20 × 20 cm) were coated with a 0.3 mm layer of silica gel (Merck Kieselgel PF 254-366) and activated at 110° for 1 h. One reverse phase system was used in which the activated plates were impregnated by allowing a 5% v/v solution of liquid paraffin BP in hexane to run to the top of the plate. The solvent was evaporated at 40°.

The developing solvents evaluated were:

- (1) Chloroform
- (2) Dichloromethane
- (3) Diethyl ether
- (4) Dichloromethane-diisopropyl ether (4:1)
- (5) Chloroform-ethanol (19:1)<sup>8</sup>
- (6) Dichloromethane-ethanol (19:1)<sup>8</sup>
- (7) Chloroform-acetone (9:1)<sup>7</sup>
- (8) Chloroform-acetone (7:3)<sup>7</sup>
- (9) Hexane-acetone (9:1)<sup>7</sup>
- (10) Hexane-acetone (7:3)<sup>7</sup>
- (11) Acetone-*n*-hexane-benzene (1:2:5)<sup>10</sup>
- (12) Chloroform-nitromethane (1:1)<sup>11</sup>
- (13) Chloroform-glacial acetic acid (60:1)<sup>9</sup>
- (14) Ethanol-water (4:6) with paraffin impregnated plates<sup>14</sup>

Spots of solution (5 μl) containing 5 μg of each herbicide were applied 2 cm from the edge of the plates. The solvents were allowed to run for 15 cm after which the plates were dried and viewed under UV light from a Hanovia "Chromatolite".

TABLE I  
TLC  $R_F$  VALUES AND GAS CHROMATOGRAPHIC RETENTION TIMES FOR ELEVEN UREA HERBICIDES

System	Fluometuron	Mono-linuron	Buturon	Monuron	Metobromuron	Diuron	Linuron	Metoxymarc	Neburon	Benzomarc	Chlorbromuron
1	0.14	0.48	0.15	0.12	0.51	0.14	0.58	0.13	0.38	0.14	0.56
2	0.07	0.24	0.19	0.06	0.25	0.07	0.32	0.07	0.17	0.07	0.33
3	0.22	0.48	0.53	0.15	0.51	0.16	0.51	0.16	0.50	0.15	0.52
4	0.21	0.58	0.57	0.18	0.59	0.20	0.62	0.21	0.54	0.19	0.63
5	0.43	0.71	0.66	0.42	0.72	0.42	0.72	0.42	0.68	0.70	0.72
6	0.50	0.63	0.57	0.49	0.61	0.51	0.68	0.44	0.61	0.48	0.73
7	0.39	0.62	0.60	0.33	0.64	0.39	0.68	0.38	0.59	0.34	0.68
8	0.58	0.70	0.75	0.51	0.72	0.58	0.74	0.57	0.75	0.58	0.74
9	0.04	0.11	0.07	0.03	0.11	0.04	0.11	0.04	0.10	0.05	0.10
10	0.34	0.44	0.40	0.27	0.43	0.34	0.48	0.33	0.49	0.35	0.48
11	0.15	0.41	0.44	0.11	0.43	0.17	0.44	0.13	0.38	0.14	0.44
12	0.63	0.81	0.84	0.54	0.82	0.64	0.86	0.64	0.85	0.78	0.85
13	0.22	0.38	0.31	0.22	0.38	0.22	0.43	0.23	0.32	0.30	0.46
14	0.53	0.58	0.54	0.60	0.53	0.46	0.41	0.44	0.48	0.42	0.38
GC retention times (min)	0.24	0.49	0.50	0.51	0.68	0.95	0.95	0.95	0.95	0.97	1.39

### Results and discussion

The  $R_F$  values obtained are given in Table I, together with the retention times for the gas chromatographic system reported by MCKONE AND HANCE<sup>12</sup>. The best resolutions obtained by the thin-layer systems were given by solvents 1, 2, 10, 13, 14 each of which could resolve a mixture of all the ureas into four groups. Of these systems 13 and 14 are probably best. The four groups produced by system 13 contain (a) fluometuron, monuron, diuron, Metoxymarc; (b) buturon, neburon, Benzomarc; (c) monolinuron, metobromuron; (d) linuron, chlorbromuron, while the groups produced by system 14 contain (a) neburon; (b) diuron, linuron, Metoxymarc, Benzomarc, chlorbromuron; (c) fluometuron, buturon, metobromuron; (d) monolinuron, monuron.

Thus the use of these two chromatographic systems would allow the identification of any of the ureas except that diuron cannot be resolved from Metoxymarc and linuron cannot be resolved from chlorbromuron. None of the thin-layer systems studied will resolve these two pairs. However, if the gas chromatographic system is also used then linuron and chlorbromuron can be separated although diuron and Metoxymarc would still not be resolved.

Using the extraction procedure of MCKONE<sup>13</sup> levels of 0.5 p.p.m. may be easily visualised on thin-layer plates and for soils low in organic matter the limit of detection is 0.1 p.p.m. or less.

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