

CHROM. 9832

## Note

### Reversed-phase high-performance liquid chromatography of some common herbicides

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(Received November 19th, 1976)

Currently high-performance liquid chromatography (HPLC) is assuming a growing importance in the analysis of organic compounds including pesticide residues<sup>1</sup>. In this laboratory HPLC has proved useful in the estimation of herbicide residues in soil and water samples. This paper summarises our experience to date.

#### EXPERIMENTAL

##### *Apparatus*

Perkin-Elmer Model 1240 liquid chromatograph fitted with a Cecil 212 variable-wavelength UV monitor was used.

##### *Herbicides*

Table I lists the herbicides studied.

TABLE I  
HERBICIDES STUDIED

<i>Name</i>	<i>Chemical name</i>
Bromacil	5-bromo-6-methyl-3-(1-methylpropyl)-uracil
Lenacil	2,4-(3H,5H)-dione-3-cyclohexyl-6,7-dihydro-1H-cyclopentapyrimidine
Terbacil	5-chloro-6-methyl-3- <i>tert.</i> -butyl uracil
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
Cyanatryn	3-(1-cyano-1-methylethylamino)-4-ethylamino-6-methylthio-1,3,5-triazine
Simazine	2-chloro-4,6-bisethylamino-1,3,5-triazine
Terbutryne	4-ethylamino-2-methylthio-6- <i>tert.</i> -butylamino-1,3,5-triazine
Velpar (DP 3674)	3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione
Chlortoluron	N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea
Isoproturon	N'-(4-isopropylphenyl)-N,N-dimethylurea
Linuron	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
Methabenzthiazuron	N-(benzothiazol-2-yl)-N,N'-dimethylurea
Monuron	N'-(4-chlorophenyl)-N,N-dimethylurea
Ethofumesate	2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl-methyl sulphonate
Pyrazone	5-amino-4-chloro-2-phenylpyridazin-3-one

### Chromatography

The standard procedure in this laboratory uses reversed-phase isocratic conditions with a bonded phase packing (PE C<sub>18</sub> Sil-X-11) in a 0.5 m × 1.7 mm I.D. stainless-steel column. A range of mixtures of methanol and water have proved satisfactory as eluants (see Table II). A chart speed of 120 mm/h and an eluant flow-rate of 0.5 ml/min are used for all the separations. The injection volume is 5  $\mu$ l. The other conditions are listed in Table II.

The optimum absorption wavelength is determined by scanning a methanolic solution of the compound between 200 and 300 nm prior to chromatography.

TABLE II  
SUMMARY OF CHROMATOGRAPHIC CONDITIONS

<i>Herbicide</i>	<i>Retention time (sec)</i>	<i>Column temperature (°C)</i>	<i>Eluent (% methanol in water)</i>	<i>UV wavelength (nm)</i>	<i>f.s.d.<sub>50</sub> (ng)* (0.01 a.u.f.s.d.)**</i>
Bromacil	198	60	10	280	30
Lenacil	165	60	20	270	35
Terbacil	210	60	10	280	36
Atrazine	207	60	20	220	7
Cyanatryn	195	65	20	220	15
Simazine	195	60	20	220	6
Terbutryne	183	60	50	227	7
Velpar	168	60	20	245	20
Chlortoluron	192	60	20	215	7
Isoproturon	201	70	20	240	13
Linuron	309	65	20	250	17
Methabenzthiazuron	186	65	20	225	8
Monuron	186	40	20	250	19
Ethofumesate	225	60	25	225	57
Pyrazone	171	60	2.5	230	12

\* ng of the compounds required to produce 50% f.s.d. on recorder.

\*\* Absorption units for full scale deflection.

### RESULTS AND DISCUSSION

Methods using different HPLC systems have been published for some of the compounds dealt with here<sup>1-3</sup>. Our aim has been to develop a simple method that can be applied, with modification, to a wide range of compounds. We have found HPLC particularly useful for estimating compounds that are difficult to handle by gas-liquid chromatography (GLC) including the non-electron capturing urea isoproturon, the uracils, and the triazine herbicide cyanatryn, which tends to degrade on the column.

HPLC has advantages over GLC in the analysis of other ureas. It has been pointed out that phenylureas degrade to the isocyanates under the conditions normally used for GLC<sup>4</sup>. This does not occur with HPLC, so urea herbicides can be separated from some of their metabolites. For example, the separation of chlortoluron from two of its metabolites is shown in Table III, but with the conditions described the parent aniline 4-amino-2-chlorotoluene elutes with chlortoluron.

TABLE III

## SEPARATION OF CHLORTOLURON FROM TWO OF ITS METABOLITES

Eluant, 15% methanol in water; other conditions, as given in Table II for chlortoluron.

<i>Compound</i>	<i>Retention time (sec)</i>
Chlortoluron	309
N-(3-Chloro-4-methylphenyl)-N'-methylurea	204
N-(3-Chloro-4-methylphenyl)-urea	147

Work in this laboratory has been limited to UV-absorbing compounds, as UV absorption detectors are the most sensitive of the readily available detection systems. A variable-wavelength detector is considered essential. Whilst the absolute sensitivity of HPLC is not so good as that of GLC, the signal-to-noise ratio is similar. Hence the limits of detection are often comparable. For example, the triazines may be detected at about 0.05 ppm in soil and 0.001 ppm in water, figures that compare well with those attainable by gas chromatography using an alkali flame ionisation detector.

## ACKNOWLEDGEMENTS

The gift of herbicides from the following companies is gratefully recognised: linuron from Farbwerke Hoechst AG; monuron, bromacil, lenacil, terbacil, and Velpar from E. I. Du Pont de Nemours and Co., Inc.; simazine, and atrazine from Ciba-Geigy AG; cyanatryn from Shell Research Ltd; methabenzthiazuron from Bayer Leverkusen; ethofumesate from Fisons Ltd.

## REFERENCES

- 1 C. Self, E. H. Kerrell and T. J. N. Webber, *Proc. Anal. Div. Chem. Soc.*, Nov. (1975) 288.
- 2 J. A. Schmit, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, 1971, Coll. p. 398.
- 3 A. E. Smith and K. A. Lord, *J. Chromatogr.*, 107 (1975) 407.
- 4 D. Spengler and B. Hamroll, *J. Chromatogr.*, 49 (1970) 205.