Notes

CHROM. 3573

The gas chromatography of some substituted urea herbicides

Methods for the determination of substituted urea herbicides using gas chromatography have been reported by KIRKLAND[1], GUTENMANN AND LISK[2,3], REISER[4], WEBLEY AND MCKONE[5] and HENKEL[6]. These methods are based on the gas chromatography of the aniline derivatives of these compounds. FISHBEIN AND ZIELINSKI[7] described the behaviour of monuron and diuron on three stationary phases one of which apparently caused decomposition. Detection was by flame ionisation and no indication of sensitivity was given. The work described in this paper was undertaken to determine the conditions under which the chromatography of unchanged substituted ureas could be achieved. Twelve substituted urea herbicides containing one or more halogen atoms were examined.

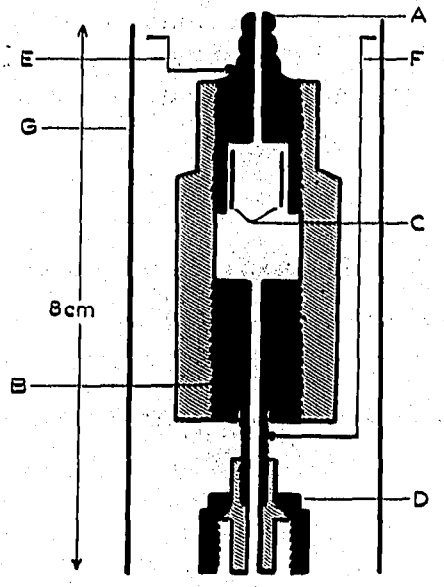

Fig. 1. Scale diagram of cross-section of the detector. A = cathode and gas exit tube 1/16 in.; B = anode; C = tritium foil 2 cm × 1 cm, 300 mC; D = standard detector base nut; E = connection to 90 V DC; F = connection to amplifier and recorder; G = standard detector cylinder. ■ = BRASS; ▨ = P.T.F.E.

Materials and methods

A Varian Aerograph 1520 gas chromatograph was used fitted with a concentric tube electron capture detector. The design of the detector (Fig. 1) is essentially the same as that previously described (MCKONE[8]), but its external configuration was modified to fit the Aerograph detector base, thus making it interchangeable with standard Aerograph detectors.

Gas chromatography

A 1.5 m × 3.5 mm O.D. stainless steel column was packed with 5 % E 301 (methyl silicone) on 60–80 mesh Gas Chrom Q. A stainless steel injector insert was used and injections were made with the tip of the needle just entering the column.

Operating conditions

Injector temperature	265°
Column temperature	150°
Detector temperature	200°
Gas flow rate	50 cc per min of oxygen-free nitrogen
Sensitivity	×1
Attenuation	8
Recorder	1 mV Leeds and Northrup Speedomax W
Detector voltage	90 V
Chart speed	30 in./h.

The following herbicides were evaluated.

Bayer 43975	N-(3,4-dichlorophenyl)-O,N',N'-trimethylisourea
Benzomarc	N-benzoyl-N-(3,4-dichlorophenyl)-N',N'-dimethylurea
buturon	N'-(4-chlorophenyl)-N-isobutynyl-N-methylurea
chlorbromuron	N-(4-bromo-3-chlorophenyl)-N'-methoxy-N'-methylurea
diuron	N'-(3,4-dichlorophenyl)-N,N-dimethylurea
fluometuron	N'-(3-trifluoromethylphenyl)-N,N-dimethylurea
linuron	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
metobromuron	N'-(4-bromophenyl)-N-methoxy-N-methylurea
Metoxymarc	N-(3,4-dichlorophenyl)-N-(4-methoxybenzoyl)-N',N'-dimethylurea
monolinuron	N'-(4-chlorophenyl)N-methoxy-N-methylurea
monuron	N'-(4-chlorophenyl)-N,N-dimethylurea
neburon	N-butyl-N'-(3,4-dichlorophenyl)-N-methylurea.

TABLE I

RETENTION TIME AND DETECTOR RESPONSE OF SOME UREA HERBICIDES USING 5 % E 301 STATIONARY PHASE ON GAS CHROM Q

Herbicide	*Retention time (min)*	*Amount (ng)*	*% F.S.D. attenuation 8*
Fluometuron	0.24	1	59
Monolinuron	0.49	2.5	2
Buturon	0.50	2.5	3.5
Monuron	0.51	2.5	4
Metobromuron	0.68	1	30.5
Diuron	0.95	1	94
Linuron	0.95	1	44.5
Metoxymarc	0.95	1	53.5
Neburon	0.95	1	70
Benzomarc	0.97	1	52
Bayer 43975	0.99	1	14
Chlorbromuron	1.39	1	35.5
3,4-Dichloroaniline	—	2.5	no peak

Standard solutions were made in 2,2,4-trimethylpentane containing 1 ng/5 μl and 2.5 ng/5 μl. A standard injection volume of 5 μl was used.

Results and discussion

The herbicides are placed in order of retention time in Table I. The compounds linuron, diuron, Metoxymarc and neburon were not resolved from each other and neither were monuron, monolinuron and buturon. The compound 3,4-dichloroaniline, included because it is a derivative of several of the substituted urea herbicides, failed to produce a response under the conditions described here. Linear relationships were obtained from 0.1 ng to 1.0 ng when the log of peak height was plotted against log nanograms of herbicide in the case of linuron, diuron, neburon, fluometuron, metobromuron, chlorbromuron, Benzomarc and Methoxymarc. Under the prescribed conditions, Bayer 43975, buturon, monuron and monolinuron gave detector responses which were considered too low to be useful for residue studies so consequently their linearity was not evaluated.

During preliminary experiments the properties of six stationary phases were examined using linuron as the test compound. They were 3 % and 10 % DC 11 (silicone grease), 5% SE 30 (methyl silicone), 5 % phenyl diethanolamine succinate, 10 % QF 1 (trifluoropropyl methyl silicone) and 5% E 301. Chromosorb W was used as the support medium. The effect of temperature in the range 140–200° was also studied. Of these stationary phases, 5 % E 301 gave the best results. Using this packing, stainless steel and glass columns were compared using both the Aerograph and the laboratory-built detectors. The results suggested that the glass columns caused some decomposition of linuron as the detector response was reduced, the peaks showed considerable tailing and subsidiary peaks appeared. There was similar evidence of decomposition in chromatograms obtained with the Aerograph detector. The different responses of the two detectors could be explained by their different geometry but the decomposition may be the result of the presence of glass in the Aerograph detector. A significant improvement in peak shape and detector response was obtained by replacing the Chromosorb W with Gas Chrom Q. A minimum injector temperature of 265° was necessary to give a reproducible peak height. Column temperatures above 150° gave increased but inconsistent peak heights with secondary peaks appearing suggesting that decomposition occurred. A gas flow of 50 cc per min produced maximum peak height. It must be emphasised that the conditions described in this work are considered optimum for linuron. Although diuron, neburon, fluometuron, metobromuron, chlorbromuron, Benzomarc and Metoxymarc also gave useful linear responses, these conditions are not necessarily the best for these herbicides.

The sensitivity of the system to these compounds is considered adequate to justify future development of residue methods based on their measurement by direct gas chromatography.

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and fluometuron—Ciba Ltd.; buturon—B.A.S.F., A.G.; Bayer 43975—Farbenfabriken Bayer A.G.; Benzomarc and Metoxymarc—Péchiney Progil.

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Theory of partition chromatography. V.

In the theory of partition chromatography developed in earlier articles[1–4], the concentration distribution and its moments were expressed as functions of the position coordinates in the column. However, in this form the theory is not applicable to normal experimental conditions, where the concentration is determined as a function of the elution volume. A modification of the theory is therefore desirable and the aim of the present article is to derive relations between the moments of the concentration distribution calculated with respect to the position coordinates in the column and those calculated with respect to the elution volume. As a rule, the notations used here are in agreement with those used in the earlier articles.

To define the problem, we consider specifically a coordinate system fixed in the column, with its x-axis parallel to the axis of the column. We assume that the exit end of the column is at the point $x = a$. We also assume that there is a concentration peak in the column, represented by the distribution function

$$c = \mathrm{f}(x,t) \tag{1}$$

We further introduce a "local" coordinate system "ξ", with its origin fixed at the mean ($x = \mu$) of the distribution. This coordinate system moves along with the peak at velocity

$$\omega = v\nu \tag{2}$$

The values of the function $\mathrm{f}(x, t)$ at an arbitrary point $x = \mu + \xi$ and at the point $x = a$ are related in the first approximation by the following transformation:

$$\mathrm{f}(x,t) = \mathrm{f}\left(a, t + \frac{a-x}{\omega}\right) - \frac{\partial \mathrm{f}(\xi,t)}{\partial t}\,\frac{a-x}{\omega} \tag{3}$$