

## Notes

CHROM. 5630

## Electrolytic conductivity detection of some nitrogen-containing herbicides

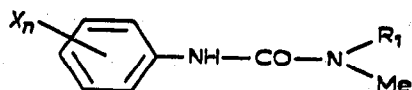
Recently the nitrogen detection limit of the Coulson electrolytic conductivity detector (CCD)<sup>1</sup> was extended down to 0.1 ng by incorporation of several refinements<sup>2</sup>. Also, the CCD detector has been used in the determination of *s*-triazine herbicides<sup>3,4</sup> and insecticides<sup>5</sup> at the ng level. As a prerequisite to regulatory analysis, this detector, incorporating most of the suggested refinements<sup>2</sup>, was evaluated for a number of *s*-triazine, substituted urea, carbamate and miscellaneous herbicides.

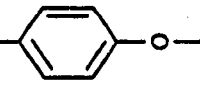
## Experimental

A Microtek MT 220 gas chromatograph fitted with a Coulson electrolytic conductivity detector Model C321 and a <sup>63</sup>Ni (14.5 mCi) electron capture detector was

TABLE I

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME SUBSTITUTED UREAS



No.	Herbicide	Structure		1/2 f.s.d. (ng)		R <sub>p</sub>	
		R <sub>1</sub>	X <sub>n</sub>	CCD	<sup>63</sup> Ni	OV-17 <sup>a</sup> at 195°	OV-17 <sup>b</sup> at 180°
1	Fluometuron	Me	3-CF <sub>3</sub>	100	—	—	0.002
2	Fenuron	Me	—	100	—	0.11	0.02S
3	Monuron	Me	4-Cl	100	1.5	0.20	0.036
4	Diuron	Me	3,4-dichloro	100	0.5	0.19	0.06
5	Neburon	<i>n</i> -Bu	3,4-dichloro	100	1.0	0.19	0.061
6	Monolinuron	OMe	4-Cl	200	5.0	0.45	0.04
7	Metobromuron	OMe	4-Br	200	0.5	0.14	0.05
8	Linuron	OMe	3,4-dichloro	200	0.5	0.19	0.06
9	Chlorbromuron	OMe	3-Cl-4-Br	200	0.4	0.22	0.09
10	Chloroxuron	Me	Cl-  -O-	200	5.0	0.83	0.72 <sup>c</sup>

<sup>a</sup> Parathion CCD retention time, 5.5 min.

<sup>b</sup> Parathion CCD retention time, 31.1 min.

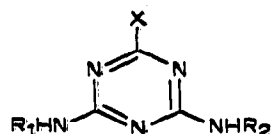
<sup>c</sup> Column temperature 225°; Parathion CCD retention time, 5.6 min.


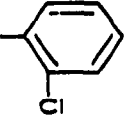
used. The 6 ft.  $\times$  6 mm O.D. glass columns were packed with 3% OV-1 on 80-100 mesh Chromosorb W HP or 5% OV-17 on 80-100 mesh Gas-Chrom Q. The operating conditions were: injector temperature, 230°; column temperature, in the range 130-225°, as indicated,  $^{63}\text{Ni}$  detector temperature, 300°; nitrogen carrier, 60 ml/min. The conductivity detector was connected by means of a 1/8 in. stainless-steel transfer line, maintained at 230°; pyrolyzer unit, 850°; helium carrier, 60 ml/min; helium sweep, 60 ml/min; hydrogen flow, 100 ml/min; DC bridge potential, 30 V; attenuator, 1. The conductivity detector also incorporated a strontium hydroxide scrubber, teflon tubing insert and 50 strand nickel wire catalyst. A 1 mV strip-chart recorder operating at 0.5 in./min was used.

Standard herbicide solutions were prepared in redistilled hexane, benzene, acetone or methanol, depending upon solubility, at a concentration of 10 mg/100 ml and serially diluted. Injection volumes of 2-10  $\mu\text{l}$  were normally employed.

TABLE II

RELATIVE RETENTION TIMES AND DETECTOR RESPONSE OF SOME S-TRIAZINES



<i>s</i> -Triazine	Structure			<i>t</i> / <i>s</i> f.s.d. (ng)		$R_p$	
	<i>X</i>	$R_1$	$R_2$	CCD	$^{63}\text{Ni}$	OV-1 at 195°	OV-17 at 225°
Simazine	Cl	Et	Et	7	2.2	0.44	0.49
Atrazine	Cl	Et	<i>i</i> -Pr	7	2.2	0.45	0.46
Propazine	Cl	<i>i</i> -Pr	<i>i</i> -Pr	7	1.1	0.45	0.43
Prometone	OMe	<i>i</i> -Pr	<i>i</i> -Pr	7	—	0.45	0.40
Bladex	Cl	Et	$-\text{C}_3\text{H}_6\text{CN}$	15	1.0	0.52	0.62
Outfox	Cl	<i>i</i> -Pr		10	2.5	0.68	0.76
Prometryne	SMe	<i>i</i> -Pr	<i>i</i> -Pr	8	50.0	0.77	0.75
Bladex metabolite	Cl	H	$-\text{C}_3\text{H}_6\text{CN}$	20	1.0	0.86	1.28
Dyrene	Cl	Cl <sup>a</sup>		200	3.0	1.14	1.28

<sup>a</sup> No NH moiety.

### Results and discussions

OV-1 was chosen as non-polar liquid phase due to its excellent thermal stability and the gas chromatographic (GC) column was operated at 195°. Similarly, the OV-17 phase also has high temperature stability and has found wide-spread use in pesticide residue analysis<sup>6,7</sup>, in particular, the organophosphorus insecticides<sup>8</sup>. As OV-17 is of intermediate polarity various column temperatures were used.

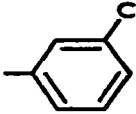
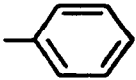
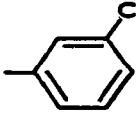
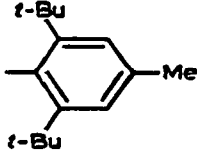
Tables I-IV show the retention times relative to parathion for various, herbicides examined. Whenever possible, a response comparison between the CCD and  $^{63}\text{Ni}$  detector, for approximate half full-scale recorder deflection (1/2 f.s.d.), was obtained.

For analysis of the substituted ureas (Table I) a column temperature of  $180^\circ$  was used. The urea herbicides were separated into two categories, based on CCD peak response. Compounds 1-5 (Table I) gave peaks with slight tailing, whereas ureas 6-9 exhibited considerable tailing (Fig. 1), hence the larger amounts required for 1/2 f.s.d. Utilization of both columns provided adequate separation for the substituted ureas, except for diuron, neburon and linuron, which were inseparable on either phase. Due to the long retention time of chloroxuron at  $180^\circ$ , analysis was performed at  $225^\circ$  without apparent decomposition.

TABLE III

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME HERBICIDAL CARBAMATES

$$R_2\text{-NH-CO-O-R}_1 \text{ AND THIOLCARBAMATES } \begin{matrix} R_2 \\ \diagdown \\ \text{N-CO-S-R}_1 \\ \diagup \\ R_3 \end{matrix} \text{ AT } 195^\circ$$

Carbamate	Structure			1/2 f.s.d. (ng)		$R_D$	
	$R_1$	$R_2$	$R_3$	CCD	$^{63}\text{Ni}$	OV-1	OV-17 <sup>a</sup>
Barban	$-\text{CH}_2\text{C}=\text{CCH}_2\text{Cl}$			70	1.5	0.17	0.02
Propham (IPC)	<i>i</i> -Pr			50	—	0.28	0.14
Chlorpropham (CIPC)	<i>i</i> -Pr			75	6.5	0.33	0.26
Azak	Me			50	—	0.72	0.62
Thiolcarbamate	Structure						
	$R_1$	$R_2$	$R_3$				
Vernam	<i>n</i> -Pr	<i>n</i> -Pr	<i>n</i> -Pr	35	—	0.22	0.12
Tillam	<i>n</i> -Pr	<i>n</i> -Bu	Et	35	—	0.22	0.12
Sutan	Et	<i>i</i> -Bu	<i>i</i> -Bu	50	—	0.25	0.10

<sup>a</sup> Parathion CCD retention time 12.9 min.

TABLE IV

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME MISCELLANEOUS PESTICIDAL COMPOUNDS AT 195°

Compound	Structure	1/2 f.s.d. (ng)		R <sub>p</sub>	
		CCD	<sup>63</sup> Ni	OV-1	OV-17
Trifluralin		25	0.7	0.31	0.19
Benefin		25	0.4	0.41	0.19
Ramrod		50	2	0.42	0.25
Diazinon		25	1.5	0.55	0.43
Propanil		100	2	0.72	0.70
Parathion		150	0.5	1.00	1.00
Diphenamid		150	—	1.08	1.35
Dacthal		—	0.5	1.09	0.90
Captan		250	2	1.22	1.7
Isocil		150	2.5	1.94 <sup>a</sup>	0.9

<sup>a</sup> With decomposition.

The *s*-triazines were gas chromatographed at 225° (Table II). On OV-17 all the *s*-triazines exhibited slight tailing. A column temperature of 200° was employed for the carbamate, thiocarbamate and miscellaneous herbicides investigated (Tables III and IV). Barban was found to display a sharp reproducible CCD peak soon after injection at 200°. With <sup>63</sup>Ni detection barban merged with the solvent front. The effect of column temperature, in the range 120–200°, on barban analysis was studied and 130° was found the most suitable for this herbicide.

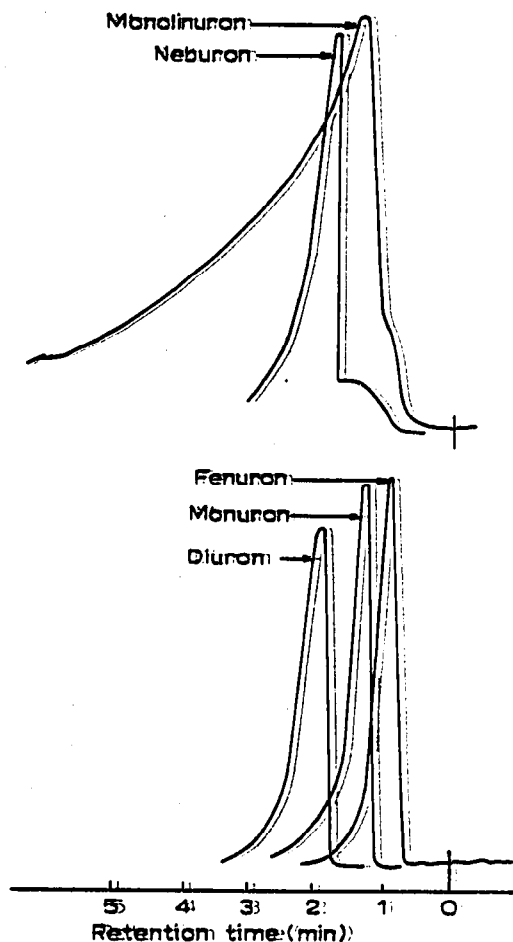


Fig. 11. Chromatogram of 4 dialkyl substituted ureas (fenuron, monuron, diuron and neburon) and 1 methyl-methoxy urea (monolinuron) on 5% OV-17 at 180° with CCD detection.

Although some herbicides and fungicides can be included in organochlorine residue analysis, *e.g.* trifluralin and captan, the use of the CCD for confirmation of identity can be a very useful adjunct. Diazinon, a two nitrogen-containing organophosphorus insecticide, was included in this study for comparison with the paration reference standard.

During the analysis of the above compounds, a number of difficulties were encountered. An array of peak slopes was obtained, and in some instances, notably the substituted ureas, reliance could not always be placed on quantitation by peak height measurements. However, quantitation was accurately accomplished via peak area measured using a digital integrator. Although the CCD is nitrogen-specific in the re-

ductive mode, initially anomalous "solvent" peaks were observed with some hexane, benzene, acetone and methanol solvents. In one instance, manograde hexane was found contaminated with acetonitrile. A different "impurity" was found in acetone, benzene and methanol from the same source. Redistillation removed the "impurity" from benzene, but not from the methanol or acetone. This "impurity" proved to be water which gave a GCD response due to leaching of basic absorbant from the fibrefrax scrubber. Water can originate from "wet" or oxygen-containing solvents.

Most injections were performed without resorting to use of the solvent vent valve. Initially, slight coking of the scrubber occurred, but no appreciable decrease in sensitivity was encountered. This appeared to result, by trial and error, from correct positioning of the teflon tubing and scrubber in relation to the red zone of the furnace block. With constant use, over a number of months, the teflon tubing showed marked accumulation of white deposits. Since these deposits contained sodium and no strontium or silicon, it was assumed they originated from continual breakdown of the quartz combustion tube. To prevent loss of sensitivity, the scrubber, silicone septum and teflon tubing were automatically replaced at two-month intervals.

Preliminary studies have been made with this gas chromatographic system for the analysis of s-triazines in water, soil and corn (to be published). No extraneous interferences were encountered from soil or water but corn extracts produced additional non-interfering peaks.

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