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Note

Gas chromatographic separation of herbicides of major interest in Canada, with electrolytic conductivity detection in the nitrogen and chlorine modes

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The great increase in herbicide use in recent years has created a need for rapid screening techniques for regulatory purposes. The present state of herbicide residue methodology by gas–liquid chromatography (GLC) lags behind the highly developed GLC residue screening techniques for most organochlorine and organophosphate insecticides. The problems associated with multi-herbicide residue analysis stem from the great differences in the chemical and physical characteristics of individual compounds. Thus most methods available to date are for single compounds or classes. Also many herbicides are not directly amenable to GLC analysis and thus must be chemically altered before gas chromatography can be carried out. This note reports on the direct GLC separation of ten herbicides (and two fungicides) of major interest in Canada. The use of the Coulson conductivity detector in the nitrogen and chlorine modes are compared. Since practically all herbicides contain nitrogen or halogens the Coulson was thought to be a good detector for multi-herbicide residue analysis. Also, its high selectivity helps reduce the sample cleanup that is required for other detectors.

EXPERIMENTAL

Reagents

Table I lists the common and chemical names of the pesticides used in this work. Stock solutions of these were prepared at 1 mg/ml in acetone. Working solutions were prepared by appropriate dilution of aliquots of the stock solutions with acetone.

Gas chromatography

A Microtek MT 220 gas chromatograph equipped with a Coulson conductivity detector was used for the analyses. The columns were 1.3 m × 6 mm O.D. borosilicate glass. The liquid phases examined were 3% OV-1, 4% SE-30–6% SP-2401, 10% DC-200 and 5% DEGS all coated on Chromosorb W HP (80–100 mesh). Column temperatures varied with liquid phase. Carrier gas (helium) flow-rate was maintained at 60 ml/min for all analyses. Operational parameters: injection port temperature, 240°; transfer line temperature, 230°; furnace temperature, 820°; helium sweep,

TABLE I

NAMES OF PESTICIDES

Common name	*Chemical name*
Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
Benzoylprop-ethyl	Ethyl-2-(N-benzoyl-3,4-dichloroanilino)propionate
Chlorpropham	Isopropyl-N-(3-chlorophenyl)carbamate
Diallate	2,3-Dichloroallyl-N,N-diisopsopylthiocarbamate
Dichlobenil	2,6-Dichlorobenzonitrile
Dicloran	2,6-Dichloro-4-nitroaniline
Dyrene	2,4-Dichloro-6-(*o*-chloroanilino)-*s*-triazine
EPTC	Ethyl-N,N-di-*n*-propylthiocarbamate
Linuron	N′-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
Propanil	N-(3,4-dichlorophenyl)propionamide
Terbacil	3-*tert*.-Butyl-5-chloro-6-methyluracil
Trifluralin	N,N-Di-*n*-propyl-2,6-dinitro-4-trifluoromethylaniline

60 ml/min; hydrogen, 50 ml/min; d.c. voltage, 30 V. The sensitivity of the Coulson detector was improved 2–3-fold by insertion of a 0.003- or 0.004-in. diameter stainless-steel wire into the capillary water entrance to the mixing chamber[1]. The nitrogen mode was used for all chromatography retention times. The chloride (reductive) mode was used with the 3% OV-1 column for determination of herbicide sensitivities. All parameters were kept the same as for the nitrogen mode; the only differences being the removal of the scrubber, nickel wire catalyst and replacement of the strong anion-exchange resin with a mixed bed (H/OH) column.

RESULTS AND DISCUSSION

Table II lists the retention times obtained for the herbicides on four different columns. OV-1 was used for initial GLC analysis. However, EPTC and dichlobenil were not separated from one another. These were separated on the DEGS column. Diallate, dicloran and atrazine which appeared close together on OV-1 were adequately separated on SE-30–SP-2401. The remaining pesticides were separated on OV-1 or DC-200.

For routine analysis OV-1 may be selected for first identification of the pesticides, then one or more of the other columns can be used for further verification.

The sensitivity of the Coulson detector in both the nitrogen and chlorine modes is presented in Table III. The sensitivities vary depending upon the percentage of nitrogen or halogens in the compounds. This response was in most cases roughly proportional to nitrogen or halogen content although results for a number of compounds were much lower than expected in the chlorine mode. This might have been due to incomplete reduction to HCl or on-column decomposition. This effect was not studied further. Compounds at longer retention times (propanil and longer) were much less sensitive in both detection modes than the earlier eluting compounds (the exception being EPTC which has no halogens and gives only a weak sulfur (H_2S) response in the chlorine mode).

For regulatory purposes sensitivity is not of prime importance since herbicide

TABLE II

RETENTION TIMES OF HERBICIDES ON FOUR COLUMNS (NITROGEN MODE)

Retention times are in min:sec. Dashes indicate that no injections were made.

Pesticide	*Column*				
	OV-1, 175°	*OV-1, 225°*	*DC-200, 187°*	*SE-30–SP-2401, 187°*	*DEGS, 165°*
EPTC	1:08	—	1:48	0:51	1:05
Dichlobenil	1:08	—	1:46	1:08	3:14
Chlorpropham	2:34	—	4:10	2:05	—
Trifluralin	2:53	—	4:45	3:01	—
Diallate	3:14	—	5:28	2:10	—
Dicloran	3:15	—	5:15	3:18	—
Atrazine	3:27	1:01	5:53	2:45	—
Propanil	5:10	—	9:39	5:30	—
Terbacil	6:17	1:45	12:25	4:30	—
Linuron	7:10	—	23:30	6:09	—
Dyrene	9:55	2:07	17:02	6:32	—
Benzoylprop-ethyl	>20:00	5:32	—	—	—

TABLE III

COULSON DETECTOR SENSITIVITY TO PESTICIDES

Sensitivities are measured at the retention times shown in Table II for OV-1 at 175° unless stated otherwise) as the number of ngrams required to produce 50% full-scale deflection.

Pesticide	*Nitrogen mode*	*Chlorine mode*
EPTC	7	137
Dichlobenil	8	5
Chlorpropham	14	38
Trifluralin	6	3
Diallate	12	2
Dicloran	7	14
Atrazine	3	6
Propanil	60	45
Terbacil	100	34
Linuron	100	250
Dyrene	60 (225°)	32
Benzoylprop-ethyl	50 (225°)	25

tolerances or actionable levels are normally in the order of 0.1–10 ppm. Thus the sensitivities reported in Table III are adequate for screening purposes. The Coulson detector, unlike many other detectors is capable of operating routinely at maximum sensitivity which makes detection of most of the compounds mentioned in Table III posible at 0.1 ppm with minimal cleanup.

REFERENCE

1 J. F. Lawrence and N. P. Sen, *Anal. Chem.*, 47 (1975) 367