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DETERMINATION OF TRIAZINE HERBICIDES IN VARIOUS CROPS BY CAPILLARY GAS CHROMATOGRAPHY WITH THERMIONIC DETECTION

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SUMMARY

The qualitative and quantitative analysis of triazine herbicides by gas chromatography was studied using packed and capillary columns, combined with either an electrolytic conductivity detector or a thermionic detector.

The thermionic detector was found to be about ten times more sensitive than the electrolytic conductivity detector; with a capillary column the sensitivity was about five times greater than with a packed column. The best separation between the triazines was obtained on a capillary column, coated with OV-225 or Carbowax 20M. The former column has the disadvantage of giving a very high background signal on the thermionic detector, so the best results were obtained with a capillary column, coated with Carbowax 20M, using a thermionic detector. In this system seven widely used triazines were easily separated completely, while the detection limit was about 10 pg.

The same system was used for a determination of triazine herbicides in various crops. The samples were first macerated with dichloromethane and the extracts then analysed as above, if necessary after clean-up over a silica gel column. The clean-up is necessary for the various kinds of cabbage, but not for other crops, such as onion and leak.

The recovery of the triazines is generally around 100% in the concentration range studied (0.02–1.0 mg/kg), and the limit of detection is less than 0.01 mg/kg.

INTRODUCTION

Triazines are among the most widely used herbicides and some of them are rather persistent in the environment. For this reason it is necessary to be able to determine residues of these compounds in different materials such as soil, water and plant materials.

Gas–liquid chromatography on packed columns has been used extensively for this purpose, with various detectors such as the electrolytic conductivity detector[1–5], the electron-capture detector[2] and the thermionic detector[3,6]. High-performance liquid

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chromatography has also been employed in the analysis of triazines[7,8], although not for residue analysis. Recently, the use of capillary gas chromatography (GC) for the separation of triazine herbicides has been studied[9]. With this technique it is possible to separate most of the triazines in use at present, which allows the determination of triazine residues in samples of unknown history.

In this paper we compare the use of packed and capillary columns, and of two different detectors. We also describe a method for the determination of triazine herbicides in various crops, using a capillary column and a thermionic detector.

EXPERIMENTAL

Apparatus

GC on packed columns was carried out using a Tracor 550 gas chromatograph, equipped with a Tracor 702 thermionic detector and a Tracor 310 electrolytic conductivity detector. The glass column (120 cm × 3 mm I.D.) was packed with 5% Carbowax 20M on Chromosorb W HP, 80–100 mesh. For the experiments with the thermionic detector the conditions were as follows: column temperature 220°C; injector temperature 240°C; detector temperature 250°C; carrier gas (nitrogen) flow-rate 30 ml/min; air flow-rate 120 ml/min; hydrogen flow-rate 3 ml/min. For the experiments with the electrolyte conductivity detector the conditions were: column temperature 235°C; injector temperature 240°C; furnace temperature 900°C; carrier gas (helium) flow-rate 50 ml/min; reaction gas (hydrogen) flow-rate 70 ml/min.

GC on capillary columns was carried out using a Hewlett-Packard 5730 A chromatograph, equipped with a HP 18740 B capillary inlet system and a HP 18789 A thermionic detector. The column (12 m × 0.3 mm I.D.) was coated dynamically with Carbowax 20M. The conditions were as follows: column temperature programmed from 120 to 220°C at a rate of 15°C min; injector temperature 240°C; detector temperature 250°C; carrier gas (helium) column-head pressure 15 p.s.i.; purge gas (helium) flow-rate 50 ml/min; air flow-rate 50 ml/min; hydrogen flow-rate 3 ml/min.

The same instrument was used with a capillary column (40 m × 0.3 mm I.D.) coated dynamically with OV-225. In this case the column temperature was programmed from 120 to 220°C at a rate of 10°C/min, the other conditions being the same as with the capillary Carbowax 20M column.

Reagents

Acetone ("zur Analyse") and silica gel 60 were obtained from E. Merck (Darmstadt, G.F.R.), dichloromethane (distilled prior to use) from Brocacef (Maarssen, The Netherlands) and anhydrous sodium sulphate (AnalaR) from BDH (Poole, Great Britain). Silica gel was dried at 200°C for at least 8 h and allowed to cool in a desiccator for 30 min prior to use; sodium sulphate was dried for 3 h at 500°C.

Procedures

Extraction. A 100-g sample was cut into small pieces and macerated with 200 ml of dichloromethane. After centrifugation the extract was transferred into a beaker and the sample was again macerated with 200 ml of dichloromethane. The two extracts were combined, the aqueous layer was decanted off and the organic phase was dried over sodium sulphate and transferred into a graduated cylinder. An

aliquot, corresponding to 25 g of sample, was then evaporated to 5 ml in a Kuderna Danish apparatus.

Clean-up. In a chromatographic tube, 23 cm × 6 mm I.D., was put a plug of glass wool, followed by a layer of sodium sulphate and 1 g of silica gel, covered with another layer of sodium sulphate. A 1-ml volume of the concentrated extract was placed on top of this column with the aid of 2 ml of dichloromethane. The column was then washed with 15 ml of dichloromethane, containing 0.5% (v/v) of acetone, and the eluate was discarded. The compounds were eluted with 10 ml of dichloromethane, containing 15% (v/v) of acetone, and the eluate was collected and evaporated to 1 ml. A 1-μl volume was injected into the gas chromatograph, using the capillary Carbowax 20M column and thermionic detector.

RESULTS AND DISCUSSION

In order to find the best column for separation of the triazine herbicides their retention times on various columns were determined, and are given in Table I. It can be seen that the capillary Carbowax 20M and OV-225 columns are equivalent in resolving power, but the OV-225 column has the advantage of giving much shorter retention times for methoprotryn and cyanazine. This column, however, has the disadvantage that it gives a very high background signal on the thermionic detector at temperatures of 200°C and higher, and therefore cannot be used at higher temperatures and at high sensitivities. No retention time is given for cyanazine on the packed column because this compound was not eluted within a reasonable time.

TABLE I

RETENTION TIMES OF TRIAZINES RELATIVE TO THAT OF ATRAZINE ON VARIOUS COLUMNS

The absolute retention time of atrazine is 6.5 min.

Triazine	*Packed column Carbowax 20M*	*Capillary column*	
		Carbowax 20M	*OV-225*
Propazine	0.75	0.93	0.96
Terbutylazine	0.85	1.04	0.98
Secbumeton	0.86	0.95	0.99
Atrazine	1.00	1.00	1.00
Prometryn	1.11	1.03	1.08
Terbutryn	1.24	1.04	1.10
Simazine	1.31	1.08	1.04
Ametryn	1.41	1.07	1.11
Desmetryn	1.57	1.16	1.11
Simetryn	1.79	1.18	1.16
Metribuzin	2.44	1.34	1.20
Methoprotryn	4.21	1.92	1.54
Cyanazine	—	2.53	1.71

For the triazines which are most widely used in The Netherlands, the limits of detection were determined on various columns with two different detectors; the results are given in Table II. It is seen that with a thermionic detector and a packed column the sensitivity is 7–10 times better than with an electrolytic conductivity detector and

TABLE II

LIMITS OF DETECTION (pg) FOR TRIAZINES ON PACKED AND CAPILLARY COLUMNS WITH DIFFERENT DETECTORS

Triazine	*Packed column*		*Capillary column, thermionic detector*
	Electrolytic conductivity detector	*Thermionic detector*	
Propazine	300	30	10
Atrazine	400	40	10
Simazine	300	40	8
Prometryn	300	45	10
Desmetryn	400	40	10
Methoproptryn	1000	150	40
Cyanazine	—	—	40

a packed column. When using a thermionic detector the sensitivity with a capillary column is about five times better than the sensitivity with a packed column.

Chromatograms obtained by injection of crude extracts of blank samples showed that there is little or no interference from crops such as onion, leak, peas, beans and rye. This is illustrated in Fig. 1 for a blank onion sample, spiked to a con-

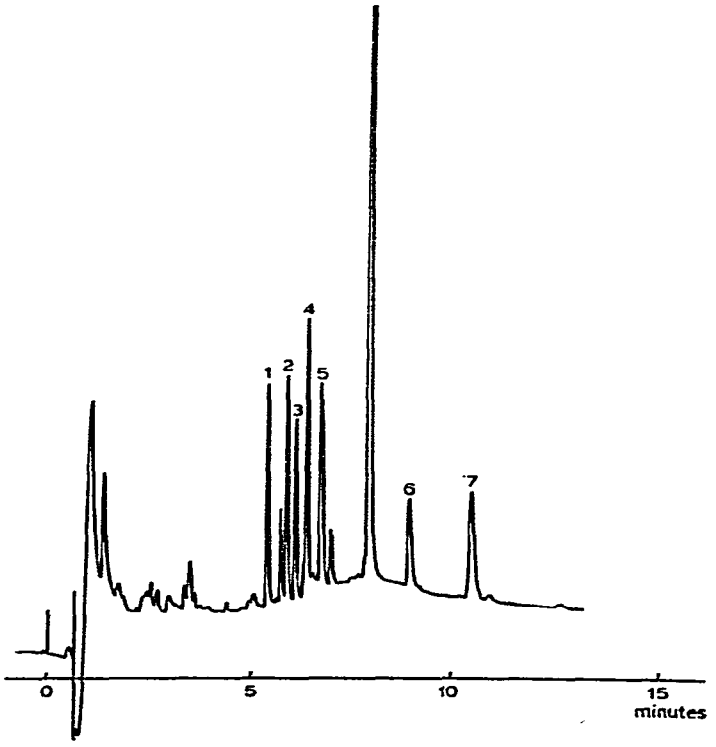

Fig. 1. Chromatogram of a blank onion sample, spiked to a concentration of 0.1 mg/kg. Peaks: 1 = propazine; 2 = atrazine; 3 = simazine; 4 = prometryn; 5 = desmetryn; 6 = methoprotryn 7 = cyanazine.

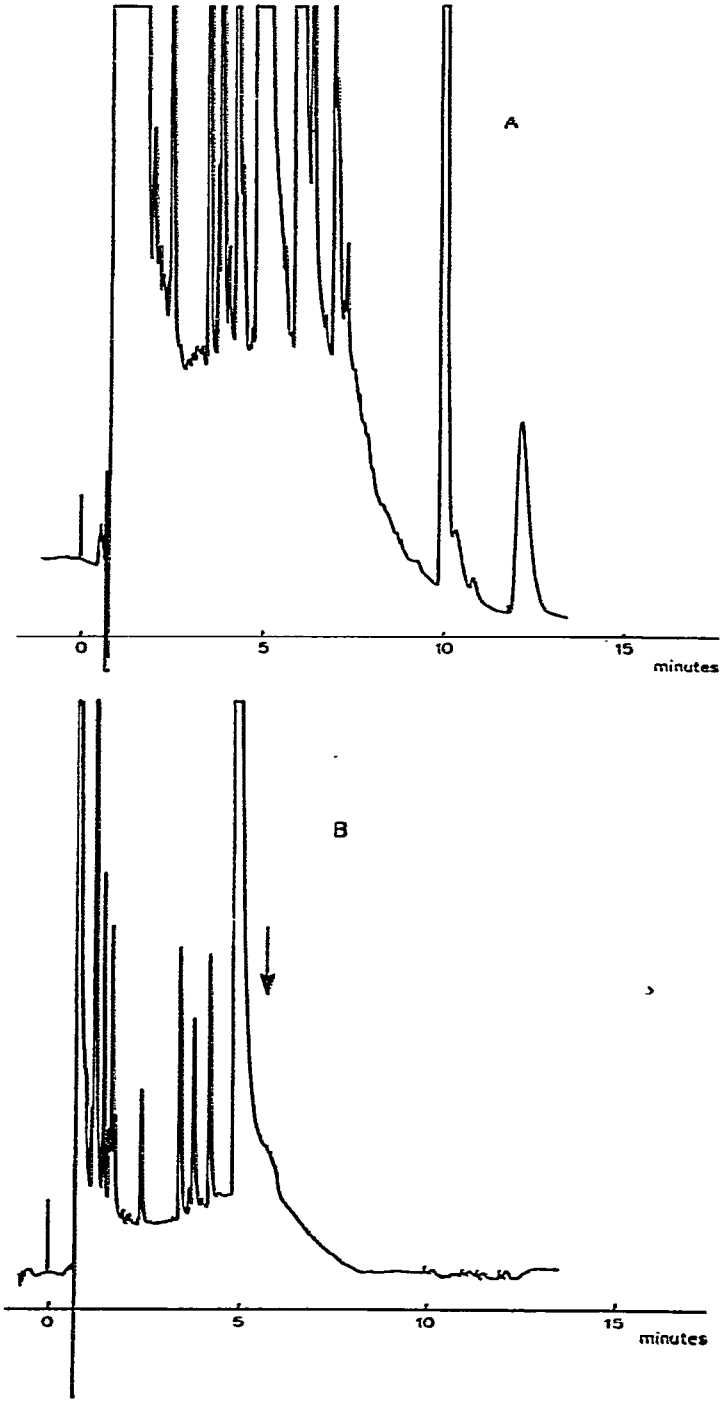

Fig. 2. Chromatograms of a blank white cabbage sample, before (A) and after (B) clean-up of the extract as described under *Procedures*. The sensitivity is such that a concentration of 0.05 mg/kg would give 50% full scale deflection; the arrow indicates the retention time of the first compound eluted.

centration of 0.1 mg/kg. At this concentration the triazines can be determined without any clean-up of the extract. For some other crops, especially the various kinds of cabbage, many interfering peaks appear in the chromatograms of blank extracts, as is shown in Fig. 2. In this figure the effect of a clean-up as described under *Procedures* is also shown and it is clear that after this clean-up the determination of triazines in cabbage can readily be carried out.

Table III gives the results of recovery studies of the triazines at a level of 0.1 mg/kg in some crops without clean-up of the extract. The mean recoveries and coefficients of variation are also given. In all cases the recovery is better than 90%, while the coefficient of variation is less than 10%, so good results are obtained for these crops at this concentration level, which is the Maximum Residue Limit for most of these pesticides. At lower levels interferences might occur, in which case a clean-up of the extracts would be necessary.

TABLE III

RECOVERIES (%) OF TRIAZINES IN VARIOUS CROPS, DETERMINED WITHOUT CLEAN-UP OF THE EXTRACT

The amount added corresponds to a residue of 0.1 mg/kg. Each value is the mean of two determinations.

Triazine	*Leak*	*Peas*	*Rye*	*Onion*	*Average*	*Coefficient of variation*
Propazine	96	102	106	97	100	5
Atrazine	96	101	111	101	102	6
Prometryn	97	97	97	87	95	5
Simazine	98	99	104	97	100	3
Desmetryn	101	101	103	96	100	3
Methoprotryn	93	97	98	87	94	6
Cyanazine	89	85	103	88	94	8

The results of recovery studies at three different levels in some kinds of cabbage are given in Tables IV–VI. In these cases the complete procedure, including the clean-up step, was used. The mean recoveries and coefficients of variation are also given. At the levels of 1.0 and 0.1 mg/kg the recoveries are around 100%, while the coefficient

TABLE IV

RECOVERIES (%) OF TRIAZINES IN VARIOUS KINDS OF CABBAGE, USING THE COMPLETE PROCEDURE

The amount added corresponds to a residue of 1 mg/kg; for methoprotryn and cyanazine the concentration is 4 mg/kg.

Triazine	*White cabbage*	*Green cabbage*	*Chinese cabbage*	*Red cabbage*	*Average*	*Coefficient of variation*
Propazine	87	88	97	88	90	5
Atrazine	86	87	98	93	91	6
Prometryn	84	100	98	116	100	13
Simazine	85	94	102	105	97	9
Desmetryn	85	97	98	108	97	10
Methoprotryn	96	110	99	111	104	11
Cyanazine	89	103	103	124	105	17

TABLE V

RECOVERIES (%) OF TRIAZINES IN VARIOUS KINDS OF CABBAGE, USING THE COMPLETE PROCEDURE

The amount added corresponds to a residue of 0.1 mg/kg; for methoprotryn and cyanazine the concentration is 0.4 mg/kg.

Triazine	*White cabbage*	*Green cabbage*	*Chinese cabbage*	*Red cabbage*	*Average*	*Coefficient of variation*
Propazine	89	97	86	101	93	7
Atrazine	93	103	103	101	100	5
Prometryn	90	94	81	93	90	6
Simazine	98	110	110	102	105	6
Desmetryn	96	103	100	94	98	4
Methoprotryn	105	96	100	81	95	10
Cyanazine	112	111	120	84	107	16

TABLE VI

RECOVERIES (%) OF TRIAZINES IN VARIOUS KINDS OF CABBAGE, USING THE COMPLETE PROCEDURE

The amount added corresponds to a residue of 0.02 mg/kg; for methoprotryn and cyanazine the concentration is 0.1 mg/kg.

Triazine	*White cabbage*	*Green cabbage*	*Chinese cabbage*	*Red cabbage*	*Average*	*Coefficient of variation*
Propazine	95	105	99	97	99	5
Atrazine	102	111	117	92	106	11
Prometryn	97	100	103	—	100	3
Simazine	113	117	111	110	113	4
Desmetryn	104	114	98	106	106	9
Methoprotryn	122	122	102	94	110	14
Cyanazine	122	139	122	100	120	16

of variation is in general below 10%. For methoprotryn and cyanazine the results are less satisfactory: the sensitivity is not as good and the coefficient of variation is rather high. The same effect was observed when standard solutions were injected, so this large variation is not due to the extraction or clean-up but to the gas chromatography. The long retention time and asymmetric peak shape of these two compounds might be an explanation for this phenomenon.

The mean recoveries in Table VI are in general somewhat above 100%. An explanation for this effect might be that after injection of an extract the peaks show less tailing than after injection of a standard solution, so that in the former case higher peaks are obtained than in the latter. No value is given for the recovery of prometryn from red cabbage at 0.02 mg/kg because for some red cabbage samples a large peak occurred, very close to the prometryn peak, which made quantification of prometryn impossible.

The coefficient of variation at a level of 0.02 mg/kg, given in Table VI, is still quite good for most compounds so the limit of detection for these compounds is well below 0.01 mg/kg. For methoprotryn and cyanazine the detection limit is higher, but at the level of 0.1 mg/kg the signal-to-noise ratio is still greater than 15, so the limit of detection is at least 0.02 mg/kg.

For most triazines the Maximum Residue Limit in The Netherlands is 0.1 or 0.05 mg/kg, so the method has an adequate sensitivity for regulatory purposes and use in monitoring programs.

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