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Note

Separation of multi-component mixtures of N-dealkylated degradation products of *s*-triazine herbicides and their parent compounds by glass capillary gas-liquid chromatography

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The degradation of *s*-triazines, which have been used in large amounts as herbicides, is caused by soil physicochemical factors, biological systems (plants, microorganisms, animals) and irradiation. Three major degradation pathways are evident: hydrolysis at the C-2 position, by which non-phytotoxic products are obtained, N-dealkylation at the C-4 and C-6 positions, by which less phytotoxic products could be obtained, and splitting of the triazine ring¹.

Although gas-liquid chromatography (GLC) has been employed successfully for the analysis of the parent compounds^{2,3}, hydroxy-*s*-triazines are highly polar, non-volatile and cannot be analysed directly by GLC but only after silylation⁴⁻⁶ or methylation⁶. The advantage of the methylation procedure is that the methylated products can be separated under the same GLC conditions as the parent compounds.

Shimabukuro and co-workers⁷⁻⁹ investigated the nature of the dealkylation of atrazine by GLC. Sirons *et al.*¹⁰ and Muir and Baker¹¹ determined residues of some dealkylated *s*-triazines and their parent compounds in water and soil by GLC on packed columns.

The above methods, all of which involved the use of packed columns, however, do not resolve adequately complex mixtures of *s*-triazines. In order to obtain better separations we have recently introduced high-resolution glass capillary columns for the analysis of multi-component mixtures of chloro-, methoxy- and methylthio-*s*-triazines^{12,13}. The aim of this work was to extend the use of capillary columns to the separation of mixtures of N-dealkylated *s*-triazines and their parent compounds. Twenty-nine *s*-triazines and their N-dealkylated degradation products were separated on a Carbowax 20M glass capillary column at 473°K.

EXPERIMENTAL

Chemicals

The common or trade names of the *s*-triazines studied and their N-dealkylated degradation products are given in Tables I and II. Many *s*-triazines and all degradation products were standard materials obtained from Ciba-Geigy (Basle, Switzerland). Solutions of 5 mg of *s*-triazines in 10 ml of chloroform were used for analysis.

Solutions of 5 mg of N-dealkylated degradation products (A,B,C,D,E,F,G,H and K) were prepared in ethyl acetate or chloroform. Saturated solutions of the standard M in dioxane and standards I, J, L and N in methanol were used.

Apparatus

A Carlo Erba Model 2350 gas chromatograph equipped with a flame-ionization detector and a stream splitter was used. The thermostat was maintained at 473°K and the injection block temperature was 548°K.

Glass capillary columns were made of Unihost soft soda-lime glass (Jablonec Glass Works, Jablonec, Czechoslovakia). We have previously described surface roughening, coating procedures and column conditioning¹⁴. A glass capillary column (54.3 m × 0.25 mm I.D.) dynamically coated with 5% Carbowax 20M was used with nitrogen as carrier gas at a pressure of 187.4 kPa. The inner surface of the column was deactivated with a thin layer of non-extractable Carbowax 20M¹⁵. To shorten the time of analysis a short column (11.0 m × 0.24 mm I.D.), cut from an originally long column dynamically coated with 10% Carbowax 20M at a nitrogen pressure of 35.5 kPa, was also used. A volume of 1 μ l of standard solution was injected with a splitting ratio of 1:100.

Methane was used for the dead-time determination. The retention times were measured with a stop-watch.

RESULTS AND DISCUSSION

As complex mixtures of herbicides and their degradation products can be expected in the analysis of environmental samples (residues in soil, water and different biological or agricultural materials), for the separation of N-dealkylated degradation products of *s*-triazine herbicides and their parent compounds we utilized high-resolution glass capillary columns coated with Carbowax 20M. We have previously demonstrated¹²⁻¹⁴ that glass capillary columns with this liquid stationary phase are very convenient for the analysis of *s*-triazines.

The separations of different mixtures on the longer column are shown in Figs. 1 and 2. As the retention times of certain compounds were long and the analysis on this column required more than 1 h, for further analysis we have used the shorter column, and typical results are shown in Fig. 3. The retention times and capacity ratios of *s*-triazines and N-dealkylated degradation products under the same experimental conditions are given in Tables I and II. Relative retentions are given in Table III.

Comparison of the data in Tables I-III with those in the chromatogram in Fig. 3 shows that some peaks of *s*-triazines and degradation products overlap. The analysis was performed without optimizing the temperature or carrier gas velocity. In a single analysis of 15 *s*-triazines and their N-dealkylated degradation products it was not possible to separate two pairs of *s*-triazines and degradation products (9+A, 14+E) and two pairs of degradation products (C+D, H+I). In the separation of *s*-triazines that differ only in the substituent in the 2-position (*e.g.* atraton, atrazine, ametryn) and all their degradation products the results were good.

With given substituents on amino groups at the 4- and 6-positions, *s*-triazines elute in the order of 2-methoxy-, 2-chloro- and 2-methylthio-*s*-triazines¹², and the same

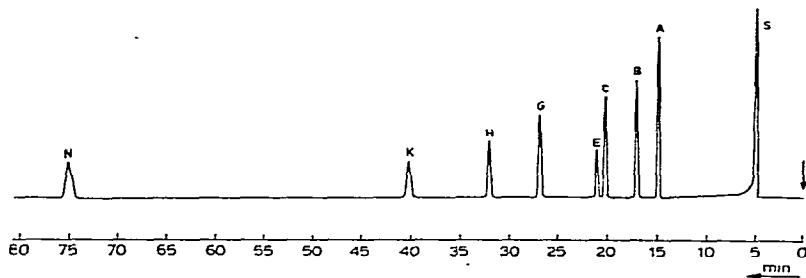


Fig. 1. Separation of some N-dealkylated degradation products of *s*-triazines on a 54.3-m Carbowax 20M glass capillary column at 473°K.

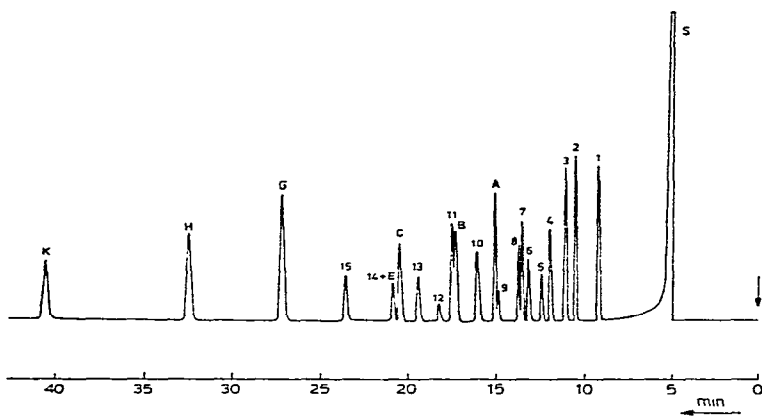


Fig. 2. Separation of a mixture of *s*-triazines and N-dealkylated degradation products on a 54.3-m Carbowax 20M glass capillary column at 473°K.

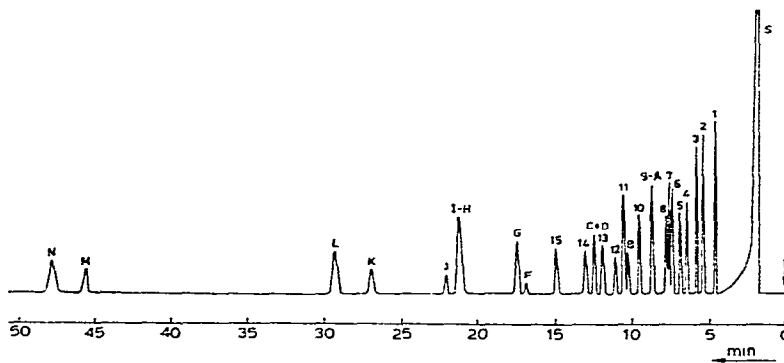
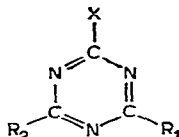


Fig. 3. Separation of a mixture of 15 *s*-triazines and 14 N-dealkylated degradation products on an 11.0-m Carbowax 20M column at 473°K.

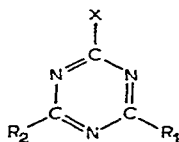
TABLE I

ADJUSTED RETENTION TIMES (t_R') AND CAPACITY RATIOS (k) OF *s*-TRIAZINES

No.*	Common and trade names	X	R ₁	R ₂	t_R' (sec)	k
1	Ipazine	Cl	N(C ₂ H ₅) ₂	NHCH(CH ₃) ₂	178.3	2.29
2	Prometon, G-31435	OCH ₃	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	229.4	2.95
3	Terbuton	OCH ₃	NHC ₂ H ₅	NHCH(CH ₃) ₃	253.7	3.26
4	Atraton, G-32293	OCH ₃	NHC ₂ H ₅	NHCH(CH ₃) ₂	292.4	3.76
5	Propazine, G-30028	Cl	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	316.0	4.06
6	Terbutylazine, GS-13529	Cl	NHC ₂ H ₅	NHC(CH ₃) ₃	350.0	4.50
7	Secbumeton, GS-14254	OCH ₃	NHC ₂ H ₅	NHCH(CH ₃)C ₂ H ₅	362.0	4.65
8	Simeton	OCH ₃	NHC ₂ H ₅	NHC ₂ H ₅	370.9	4.77
9	Atrazine, G-30027	Cl	NHC ₂ H ₅	NHCH(CH ₃) ₂	425.4	5.47
10	Prometryn, G-34161	SCH ₃	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	475.2	6.11
11	Terbutryn, GS-14260	SCH ₃	NHC ₂ H ₅	NHC(CH ₃) ₃	534.7	6.88
12	Simazine, G-27692	Cl	NHC ₂ H ₅	NHC ₂ H ₅	568.7	7.31
13	Ametryn, G-34162	SCH ₃	NHC ₂ H ₅	NHCH(CH ₃) ₂	620.1	7.97
14	Desmetryn, G-34360	SCH ₃	NHCH ₃	NHCH(CH ₃) ₂	685.6	8.81
15	Simetryn	SCH ₃	NHC ₂ H ₅	NHC ₂ H ₅	803.6	10.33

* Used in Figs. 2 and 3.

TABLE II

ADJUSTED RETENTION TIMES (t_R') AND CAPACITY RATIOS (k) OF N-DEALKYLATED DEGRADATION PRODUCTS OF *s*-TRIAZINES

No.*	Trade name	X	R ₁	R ₂	t_R' (sec)	k
A	GS-26571	OCH ₃	NHC(CH ₃) ₃	NH ₂	424.5	5.27
B	GS-14626	OCH ₃	NHCH(CH ₃) ₂	NH ₂	518.0	6.56
C	GS-25433	OCH ₃	NHCH(CH ₃)C ₂ H ₅	NH ₂	652.0	8.25
D	G-31709	OCH ₃	NHC ₂ H ₅	NH ₂	652.0	8.25
E	GS-26379	Cl	NHC(CH ₃) ₃	NH ₂	692.0	8.76
F	G-30033	Cl	NHCH(CH ₃) ₂	NH ₂	920.0	11.65
G	GS-26575	SCH ₃	NHC(CH ₃) ₃	NH ₂	952.8	12.06
H	GS-11354	SCH ₃	NHCH(CH ₃) ₂	NH ₂	1177.8	14.91
I	GS-12853	OCH ₃	NH ₂	NH ₂	1177.8	14.91
J	G-28279	Cl	NHC ₂ H ₅	NH ₂	1238.0	15.67
K	GS-11355	SCH ₃	NHC ₂ H ₅	NH ₂	1530.7	19.38
L	GS-38655	SCH ₃	NHCH ₃	NH ₂	1731.5	21.92
M	G-28273	NH ₂	NH ₂	NH ₂	2656.8	33.63
N	GS-26831	SCH ₃	NH ₂	NH ₂	2909.5	36.83

* Used in Figs. 1-3.

TABLE III

RETENTIONS OF *s*-TRIAZINES AND THEIR N-DEALKYLATED DEGRADATION PRODUCTS RELATIVE TO ATRAZINE

<i>Substance</i>	$\frac{t_{R_i'}}{t_{R'_s}}$	<i>Substance</i>	$\frac{t_{R_i'}}{t_{R'_s}}$	<i>Substance</i>	$\frac{t_{R_i'}}{t_{R'_s}}$
Prometon	0.54	Propazine	0.74	Prometryn	1.12
GS-14626	1.22	G-30033	2.16	GS-11354	2.77
GS-12853	2.77	G-28273	6.25	GS-26831	6.84
Terbuton	0.60	Terbutylazine	0.82	Terbutryn	1.26
GS-26571	1.00	GS-26379	1.63	GS-26575	2.24
G-31709	1.53	G-28279	2.91	GS-11355	3.60
GS-12853	2.77	G-28273	6.25	GS-26831	6.84
Atraton	0.69	Atrazine	1.00	Ametryn	1.46
GS-14626	1.22	G-30033	2.16	GS-11354	2.77
G-31709	1.53	G-28279	2.91	GS-11355	3.60
GS-12853	2.77	G-28273	6.25	GS-26831	6.84
Simeton	0.87	Simazine	1.34	Simetryn	1.89
G-31709	1.53	G-28279	2.91	GS-11355	3.60
GS-12853	2.77	G-28273	6.25	GS-26831	6.84
Secbumeton	0.85	Ipazine	0.42	Desmetryn	1.61
GS-25433	1.53	G-30033	2.16	GS-11354	2.77
G-31709	1.53	—	—	GS-38655	4.07
GS-12853	2.77	G-28273	6.25	GS-26831	6.84

order applies to the N-dealkylated degradation products. In analysing a mixture of *s*-triazines and N-dealkylated degradation products with the same substituent in the 2-position the undegraded substances were always eluted first. The order of elution of both parent and degraded substances shows the following pattern: the longer or the more branched is the alkyl chain bound to the amino group in the 4- or 6-position on the triazine ring, the shorter is the elution time. This effect is connected with shielding of the amino group by alkyl chains.

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