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QUALITATIVE ANALYSIS OF MULTI-COMPONENT *s*-TRIAZINE HERBICIDES BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

It has been found that in the analysis of multi-component mixtures of *s*-triazines on packed columns some problems arise in that on non-polar stationary liquids (OV-101, SE-30) many peaks of *s*-triazines overlap and some peaks are not symmetrical, depending on the support material. Separations on a polar phase (Carbowax 20M) were better, but still inadequate.

A complex mixture of chloro-, methoxy- and methylthio-*s*-triazines was separated successfully on high resolution glass capillary columns coated with Carbowax 20M. The optimal temperature for the analysis of *s*-triazines was determined from the dependence of log t_R, on $1/T$. For the characterization of *s*-triazines in environmental samples, Kováts retention indices were measured on glass capillary columns with dynamically coated non-polar (OV-101) and polar (Carbowax 20M) stationary liquids. The relationship between the structures of the *s*-triazines and their retention data was studied.

INTRODUCTION

Gas–liquid chromatography (GLC) is the most commonly used method for the analysis of *s*-triazines, which are used extensively as herbicides. GLC in packed columns has been reviewed by Cochrane and Purkayastha[1] and Fishbein[2,3]. The most frequently used stationary liquid phases in the analysis of *s*-triazines in various substrates are silicones (OV-101, SE-30, DC-200, OV-17, QF-1), polyesters (DEGS, Reoplex 400), polyethylene glycol (Carbowax 20M) and polyamide (Versamid 900). It has been shown[1,4–6] that the best separation of several *s*-triazine mixtures is accomplished on DEGS, Versamid 900 or Carbowax 20M as the stationary phase. Many workers[1–3] have successfully analysed *s*-triazines in packed columns loaded with 2–10% of Carbowax 20M. However, even on this stationary phase it is not possible to separate complex mixtures of *s*-triazines (chloro-, methoxy-, methylthio-), either isothermally or with temperature programming[7].

We have recently described the separation of *s*-triazine mixtures in glass capillary columns coated with non-polar (OV-101, SE-30), mixed (SE-30 + Carbowax

20M) and polar (Carbowax 20M) stationary phases[8]. The aim of this work was to evaluate the results obtained in the analysis of *s*-triazines in packed and glass capillary columns and to establish the relationship between the structures of *s*-triazines and their retention data.

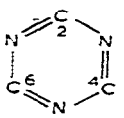
EXPERIMENTAL

Chemicals

The common and systematic names of the *s*-triazines are given in Table I. The *s*-triazines used in this work were of 98% or greater purity. Solutions of 5 mg of *s*-triazines in 10 ml of chloroform were used for analysis. The solvents used were of analytical-reagent grade and were distilled prior to use.

TABLE I

COMMON AND SYSTEMATIC NAMES OF THE *s*-TRIAZINES USED



*No.**	*Common name*	*Systematic name*
1	Ipazine	2-Chloro-4-diethylamino-6-isopropylamino-*s*-triazine
2	—	2-Chloro-4,6-bis(*tert.*-butylamino)-*s*-triazine
3	Trietazine	2-Chloro-4-diethylamino-6-ethylamino-*s*-triazine
4	Prometon	2-Methoxy-4,6-bis(isopropylamino)-*s*-triazine
5	Terbuton	2-Methoxy-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
6	Atraton	2-Methoxy-4-ethylamino-6-isopropylamino-*s*-triazine
7	Propazine	2-Chloro-4,6-bis(isopropylamino)-*s*-triazine
8	Terbutylazine	2-Chloro-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
9	Secbumeton	2-Methoxy-4-ethylamino-6-isobutylamino-*s*-triazine
10	Simeton	2-Methoxy-4,6-bis(ethylamino)-*s*-triazine
11	Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
12	Prometryn	2-Methylthio-4,6-bis(isopropylamino)-*s*-triazine
13	Terbutryn	2-Methylthio-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
14	Simazine	2-Chloro-4,6-bis(ethylamino)-*s*-triazine
15	Ametryn	2-Methylthio-4-ethylamino-6-isopropylamino-*s*-triazine
16	Desmetryn	2-Methylthio-4-methylamino-6-isopropylamino-*s*-triazine
17	Simetryn	2-Methylthio-4,6-bis(ethylamino)-*s*-triazine

* Used in Figs. 1–5.

Apparatus

Carlo Erba Model 2300 and 2350 gas chromatographs equipped with a flame-ionization detector (FID) were employed, and for glass capillaries a stream splitter was used. The narrow ends of glass capillary columns were led directly to the splitter or to the jet of the detector.

A glass column packed with 3% Carbowax 20M on 80–100-mesh Chromosorb W AW (1.3 m long and 3.3 mm I.D.) at a column temperature of 487 °K and a carrier gas (nitrogen) pressure of 253.3 kPa was used. Volumes of 2 μl of standard solutions were injected.

The glass capillary columns were made of soft soda-lime glass. We have previously described the drawing of capillaries from glass tubes, the composition of the glass[9], the surface roughening, coating procedures and column conditioning[8]. A glass capillary column coated dynamically with 29% OV-101 (69.7 m long and 0.24 mm I.D.) at column temperatures of 463, 473 and 483 °K and a carrier gas (nitrogen) pressure of 253.3 kPa, and a column coated dynamically with 10% Carbowax 20M (54.0 m long and 0.25 mm I.D.) at column temperatures of 463, 473 and 483 °K and a carrier gas (nitrogen) pressure of 152.0 kPa were used. The injector temperature was 548 °K. A volume of 1 μl of standard solution was injected with a splitting ratio of 1:100.

For the determination of Kováts retention indices, methane and alkanes were injected together with the sample of *s*-triazines. The retention times were measured with a stop-watch.

RESULTS AND DISCUSSION

The best results for the analysis of complex mixtures of *s*-triazines on either packed columns or capillary columns were obtained with Carbowax 20M as the stationary phase.

If a mixture of *s*-triazines is separated on a packed column (3% Carbowax 20M on Chromosorb W AW, 80–100 mesh, at 487 °K) all of the peaks are symmetrical, but some peaks overlap and the separation of other peaks is not to the baseline (Fig. 1). The separation of the *s*-triazine mixture on packed columns with non-polar

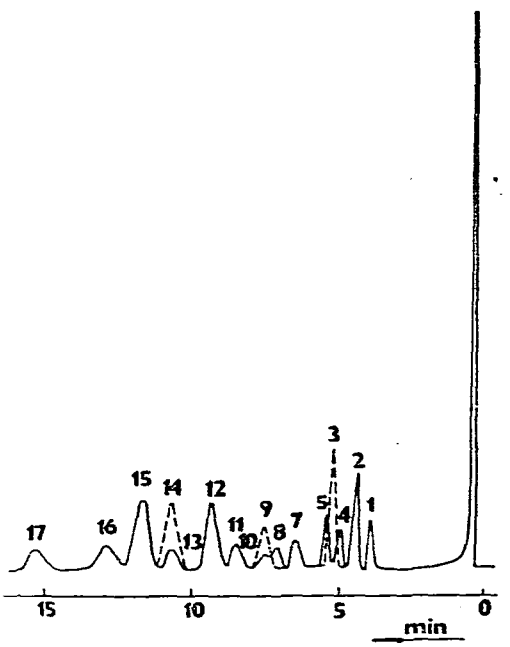


Fig. 1. Separation of *s*-triazine mixture on a column packed with 3% Carbowax 20M on Chromosorb W AW at 487 °K.

stationary phases (OV-101, SE-30) is even worse, as many more peaks overlap and some of them are non-symmetrical, depending on the support material.

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 analysis of *s*-triazines we utilized high-resolution glass capillary columns[8]. For the characterization of *s*-triazines in environmental samples, Kováts retention indices were measured on glass capillary columns with dynamically coated non-polar (OV-101) and polar (Carbowax 20M) stationary liquids.

In the analysis of complex mixtures of *s*-triazines on glass capillary columns coated with non-polar phases (OV-101, SE-30), we have demonstrated some problems that occur in the separation of 2-methoxy-*s*-triazines[8]. The separation of a model mixture of chloro- and methylthio-*s*-triazines and *n*-alkanes on a capillary column dynamically coated with OV-101 as the stationary phase at 473 °K is shown in Fig. 2.

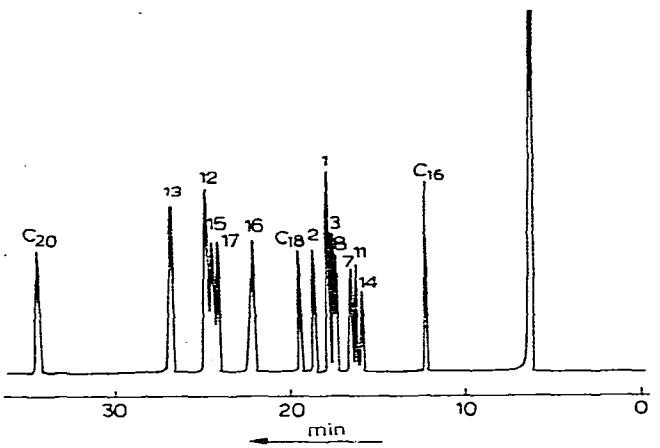


Fig. 2. Separation of chloro- and methylthio-*s*-triazines and C_{16}–C_{20} *n*-alkanes on an OV-101 glass capillary column at 473 °K.

Kováts retention indices at 463 °K and $\partial I/\partial T$ values were measured on this column (Table II). The reproducibility of the Kováts retention indices given in Table II expressed as standard deviation (s) is 0.1–0.3 index unit (four measurements). (Because of the non-symmetrical peak shapes of methoxy-*s*-triazines, the Kováts retention indices of these substances are not included in Table II.)

Kováts retention indices could be used for studying the influence of substituents in the 2-, 4- and 6-positions on the triazine ring on retention behaviour. With the same substituents at the 4- and 6-positions, chloro-*s*-triazines are eluted before the corresponding methylthio-*s*-triazines. The differences in Kováts retention indices for corresponding chloro- and methylthio-*s*-triazines (Table III) are 154–159 index units, from which it can be concluded that these differences do not depend entirely on the alkyl substituents on the amino group in the 4- and 6-positions on the *s*-triazine ring.

The $\partial I/\partial T$ values of methylthio-*s*-triazines are greater than those of the corresponding chloro-*s*-triazines (Tables II and III).

TABLE II

KOVÁTS RETENTION INDICES (*I*) AND THEIR TEMPERATURE DEPENDENCES ($\partial I/\partial T$) FOR *s*-TRIAZINES OBTAINED ON A GLASS CAPILLARY COLUMN COATED WITH OV-101 STATIONARY PHASE

No.	*Common name*	*Substituent positions*			*I (463 °K)*	*∂I (20°)*
		2-	*4-*	*6-*		
14	Simazine	Cl	NHC_2H_5	NHC_2H_5	1723.2	4.2
11	Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	1726.5	5.3
7	Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	1733.1	4.5
8	Terbutylazine	Cl	NHC_2H_5	$NHC(CH_3)_3$	1754.2	6.9
3	Trietazine	Cl	$N(C_2H_5)_2$	NHC_2H_5	1760.5	5.6
1	Ipazine	Cl	$N(C_2H_5)_2$	$NHCH(CH_3)_2$	1763.3	6.6
2	—	Cl	$NHC(CH_3)_3$	$NHC(CH_3)_3$	1781.4	6.9
16	Desmetryn	SCH_3	$NHCH_3$	$NHCH(CH_3)_2$	1847.9	3.1
17	Simetryn	SCH_3	NHC_2H_5	NHC_2H_5	1878.1	8.1
15	Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	1882.5	8.0
12	Prometryn	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	1887.7	5.3
13	Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	1912.5	8.4

TABLE III

KOVÁTS RETENTION INDICES (*I*) AND THEIR DIFFERENCES (ΔI) FOR PAIRS OF CORRESPONDING CHLORO- AND METHYLTHIO-*s*-TRIAZINES OBTAINED ON A GLASS CAPILLARY COLUMN COATED WITH OV-101 STATIONARY PHASE

No.	*Common name*	*Substituent positions*			*I (463 °K)*	*ΔI*
		2-	*4-*	*6-*		
14	Simazine	Cl	NHC_2H_5	NHC_2H_5	1723.2	
						154.9
17	Simetryn	SCH_3	NHC_2H_5	NHC_2H_5	1878.1	
11	Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	1726.5	
						156.0
15	Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	1882.5	
7	Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	1733.1	
						154.6
12	Prometryn	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	1887.7	
8	Terbutylazine	Cl	NHC_2H_5	$NHC(CH_3)_3$	1754.2	
						158.3
13	Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	1912.5	

From the results in Table II, it can be seen that with the same substituent in the 2-position the retention values of the *s*-triazines increase with increasing carbon atom number in the alkyl chain bound to the amino group in the 4- or 6-position on the triazine ring. On increasing the length of the alkyl chain by a $-CH_2-$ group, the Kováts retention indices do not increase regularly (according to Kováts' rule it should be 100 index units per $-CH_2-$ group[10]). This irregularity depends, in addition to other factors, on the alkyl chain length and on alkyl chain branching. From this behaviour it can be concluded that the retention of *s*-triazines is connected with shielding of exocyclic amino groups by alkyl groups.

We have shown that much better separations of *s*-triazines can be achieved on glass capillary columns with statically or dynamically coated Carbowax 20M as the stationary phase. The separation of a model mixture of *s*-triazines on a dynamically coated Carbowax 20M glass capillary column at 463 °K is shown in Fig. 3. All of the peaks are symmetrical. The main advantage of Carbowax 20M over OV-101 glass capillary columns is that on the former it is possible to analyse methoxy-*s*-triazines.

The optimal temperature for the analysis of *s*-triazines was determined from the dependence of log t_R, on $1/T$ (Fig. 4). From Fig. 4 it can be seen that the main problem in the separation of a model mixture of *s*-triazines is connected with trietazine and prometon. In Fig. 5 the influence of temperature on the separation of this pair of compounds is shown.

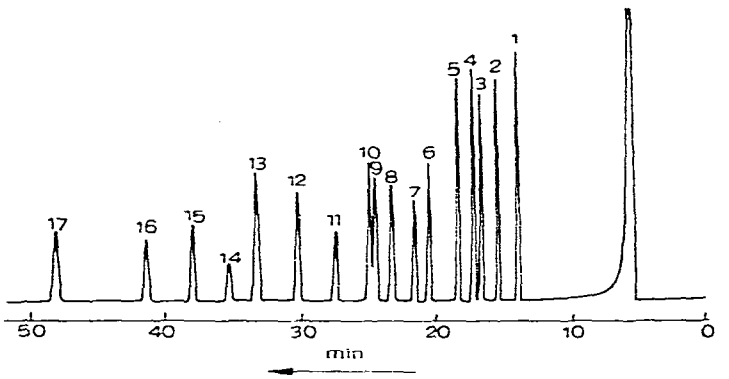


Fig. 3. Separation of *s*-triazines on a Carbowax 20M glass capillary column at 463 °K.

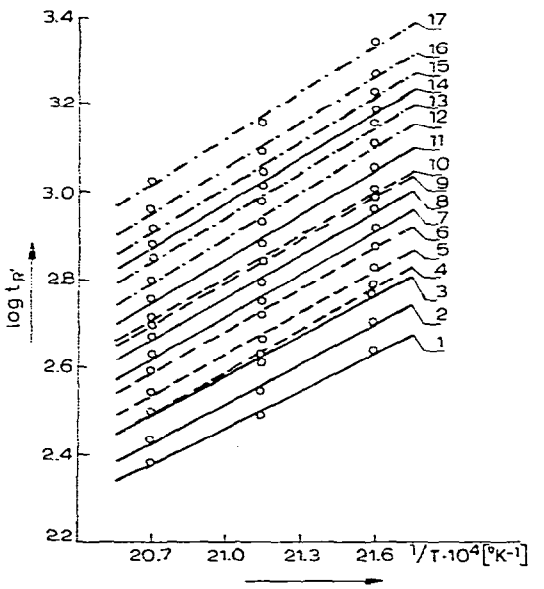


Fig. 4. Dependence of log $t_{R'}$ on $1/T$ for *s*-triazines obtained on a Carbowax 20M glass capillary column.

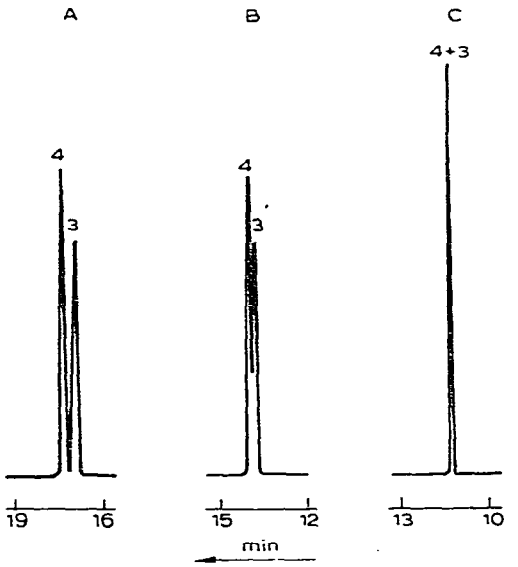


Fig. 5. Separation of the pair trietazine (3) and prometon (4) on a Carbowax 20M glass capillary column; A, 463 °K; B, 473 °K; C, 483 °K.

In Table IV Kováts retention indices measured on a Carbowax 20M glass capillary column at 463 °K, and also ∂I (20°) values, are given. The standard deviation of the Kováts retention indices obtained from four measurements for *s*-triazines on the Carbowax 20M column is 0.1–0.4 index unit. The Kováts retention indices decrease depending on the alkyl substituent and on the shielding of the amino group.

TABLE IV

KOVÁTS RETENTION INDICES (I) AND THEIR TEMPERATURE DEPENDENCES ($\partial I/\partial T$) FOR *s*-TRIAZINES OBTAINED ON A GLASS CAPILLARY COLUMN COATED WITH CARBOWAX 20M STATIONARY PHASE

No.	*Common name*	*Substituent positions*			*I (463 °K)*	*∂I (20°)*
		2-	*4-*	*6-*		
1	Ipazine	Cl	$N(C_2H_5)_2$	$NHCH(CH_3)_2$	2475.1	18.6
2	–	Cl	$NHC(CH_3)_3$	$NHC(CH_3)_2$	2518.4	14.6
3	Trietazine	Cl	$N(C_2H_5)_2$	NHC_2H_5	2559.3	20.7
7	Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2659.1	15.1
8	Terbutylazine	Cl	NHC_2H_5	$NHC(CH_3)_3$	2686.1	18.5
11	Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	2747.3	18.6
14	Simazine	Cl	NHC_2H_5	NHC_2H_5	2833.9	21.4
4	Prometon	OCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2570.3	12.1
5	Terbuton	OCH_3	NHC_2H_5	$NHC(CH_3)_3$	2597.9	15.3
6	Atraton	OCH_3	NHC_2H_5	$NHCH(CH_3)_2$	2633.4	14.4
9	Secbumeton	OCH_3	NHC_2H_5	$NHCH(CH_3)C_2H_5$	2707.8	15.1
10	Simeton	OCH_3	NHC_2H_5	NHC_2H_5	2714.1	17.9
12	Prometryn	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2779.6	19.1
13	Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	2812.1	22.8
15	Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	2859.3	22.5
16	Desmetryn	SCH_3	$NHCH_3$	$NHCH(CH_3)_2$	2888.9	25.9
17	Simetryn	SCH_3	NHC_2H_5	NHC_2H_5	2937.1	26.1

TABLE V

KOVÁTS RETENTION INDICES (I) AND THEIR TEMPERATURE DEPENDENCES ($\partial I/\partial T$) FOR METHOXY-, CHLORO- AND METHYLTHIO-*s*-TRIAZINE TRIPLETS OBTAINED ON A CARBOWAX 20M GLASS CAPILLARY COLUMN

No.	*Common name*	*Substituent positions*			*I (463 °K)*	*∂I (20°)*
		2-	*4-*	*6-*		
4	Prometon	OCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2570.3	12.1
7	Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2659.1	15.1
12	Prometryn	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2779.6	19.1
6	Atraton	OCH_3	NHC_2H_5	$NHCH(CH_3)_2$	2633.4	14.4
11	Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	2747.3	18.6
15	Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	2859.3	22.5
5	Terbuton	OCH_3	NHC_2H_5	$NHC(CH_3)_3$	2597.9	15.3
8	Terbutylazine	Cl	NHC_2H_5	$NHC(CH_3)_3$	2686.1	18.5
13	Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	2812.1	22.8
10	Simeton	OCH_3	NHC_2H_5	NHC_2H_5	2714.1	17.9
14	Simazine	Cl	NHC_2H_5	NHC_2H_5	2833.9	21.4
17	Simetryn	SCH_3	NHC_2H_5	NHC_2H_5	2937.1	26.1

Higher values of ∂I (20°) are found for trietazine, simazine, simeton and simetryn, all of which have an ethyl group bonded to amino groups at the 4- and 6-positions.

For given substituents on amino groups in the 4- and 6-positions, the Kováts retention indices and ∂I (20°) values depend on the substituent in the 2-position and increase in the order 2-methoxy-, 2-chloro- and 2-methylthio-*s*-triazines (Table V). This increase is seen in Table V for all triplets and could be used for the characterization of substituents in the 2-position in *s*-triazines.

Further characteristics that could be used for the characterization of *s*-triazines are differences in Kováts retention indices (ΔI) obtained on Carbowax 20M and OV-101 glass capillary columns. Table VI shows ΔI values of 2-chloro- and 2-methylthio-*s*-triazines at two temperatures; the values increase with increasing temperature.

TABLE VI

DIFFERENCES IN THE RETENTION INDICES (ΔI) OF CHLORO- AND METHYLTHIO-*s*-TRIAZINES ON CARBOWAX 20M AND OV-101 GLASS CAPILLARY COLUMNS

Compounds	*No.*	*Common name*	*ΔI (463 °K)*	*ΔI (483 °K)*
Chloro-*s*-triazines	14	Simazine	1110.7	1127.9
	11	Atrazine	1020.8	1034.2
	8	Terbutylazine	931.9	943.6
	7	Propazine	926.0	936.6
	3	Trietazine	798.8	813.9
	2	—	737.0	744.8
	1	Ipazine	711.8	723.8
Methylthio-*s*-triazines	17	Simetryn	1059.0	1077.0
	16	Desmetryn	1041.0	1063.8
	15	Ametryn	976.8	991.3
	13	Terbutryn	899.6	914.0
	12	Prometryn	891.9	905.7

The relationship between the reproducibility of the measurement of Kováts retention indices and the mode of preparation of glass capillary columns is currently studied and will be published later.

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