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Gas chromatographic retention indices for N-substituted amino *s*-triazines on capillary columns. Part V. Temperature dependence of the retention index

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Abstract: The temperature dependence of the retention index was studied for N-substituted amino *s*-triazines on DB-1, DB-5 and DB-WAX capillary columns within the temperature range 190–230 ºC. Two linear equations with the column temperature and its reciprocal as variables were studied. The first one shows a slightly better precision for 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines, while the second one shows a better precision for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines.

Keywords: retention indices, *s*-triazines, temperature dependence.

INTRODUCTION

The Kovats retention index I is a useful analytical tool for the identification of a compound in gas chromatography. Since these indices are not sensitive to the gas chromatographic conditions, they can be reproduced in various laboratories.

The temperature dependence of the retention data, especially of Kovats indices, has been debated for a long time.[1] The linear equations for the dependence of the retention index on column temperature t, ºC or $1/T$, K^{-1}:

$$I = a + bt \tag{1}$$

$$I = A + B/T \tag{2}$$

are valid for more or less extended temperature ranges and a variety of solutes and stationary phases. As $b = \mathrm{d}I/\mathrm{d}T$, Equation (1) corresponds (as 10 $\mathrm{d}I/\mathrm{d}T$) to the initially introduced Kovats retention index increments per 10 ºC obtained by finite differences, δI/10 ºC.

The comparative evaluation of Eqs. (1) and (2) has been considered in some papers only graphically with the conclusion that the second equation is less linear than the first one

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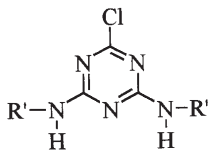
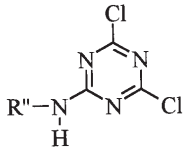
for larger temperature ranges, while some authors indicated only the δI/10 ºC of 10 dI/dT value. A comparative, detailed evaluation of Eqs. (1) and (2) was studied for perfumery compounds by Tudor.[2,3]



(I)



(II)

where R' is:
1-methylethyl (1),
1-methylpropyl (2),
1,2-dimethylpropyl (3),
1,2,2-trimethylpropyl (4),
1-methylbutyl (5),
1,3-dimethylbutyl (6),
1,3,3-trimethylbutyl (7),
1,1-dimethylpropyl (8),
1,1-dimethylbutyl (9),
1,1,3-trimethylbutyl (10),
1,1,3,3-tetramethylbutyl (11),

cyclopropyl (18),
cyclobutyl (19),
cyclopentyl (20),
cyclohexyl (21),
cycloheptyl (22),
cyclooctyl (23),
cyclononyl (24),
cyclodecyl (25),
cycloundecyl (26),
cyclododecyl (27).

and R" is:
1-methylbutyl (12),
1,3-dimethylbutyl (13),
1,1-dimethylpropyl (14),
1,1-dimethylbutyl (15),
1,1,3-trimethylbutyl (16),
1,1,3,3-tetramethylbutyl (17)

Fig. 1. Structural formulae of the 2,4-bis(alkylamino)-6-chloro-*s*-triazines (I), 2-alkylamino-4,6-dichloro-*s*-triazines (II) and 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines (I).

As part of our study[4–7] of chemical structure-retention index relationships, a study of the temperature dependence of the retention indices for a series of 27 N-substituted amino derivatives of *s*-triazines, 11 compounds of the general formula 2,4-bis(RNH)-6-Cl-*s*-triazine (di-N-substituted alkylamino derivatives of *s*-triazines), 6 compounds of the general formula 2-RNH-4,6-Cl_2-*s*-triazine (mono-N-substituted alkylamino derivatives of *s*-triazines) and 10 compounds of the general formula 2,4-bis(RNH)-6-Cl-*s*-triazine (di-N-substituted cycloalkylamino derivatives of *s*-triazines) (Fig. 1) on capillary columns of different polarity (DB-1, DB-5 and DB-WAX) is reported here.

EXPERIMENTAL

The GC analyses were performed on a Varian 3400 gas chromatograph equipped with a flame ionization detector and an all-glass split-splitless sample injector (1071 capillary injector). Data handling was provided by a Varian 4720 data system.

The capillary columns used were as follows: DB-1, obtained from J & W Scientific, Folsom, CA, USA, dimensions 30 m × 0.256 mm, film thickness 0.25 μm, theoretical plates/meter 4554 for tridecane, coating efficiency 100.3 for tridecane; DB-5, obtained from J & W Scientific, Folsom, CA, USA, dimensions 60 m ×

0.321 mm, film thickness 0.25 μm, theoretical plates/meter 3409 for tridecane, coating efficiency 94.5 for tridecane; DB-WAX, obtained from J & W Scientific, Folsom, CA, USA, dimensions 30 m × 0.234 mm, film thickness 0.25 μm, theoretical plates/meter 3260 for methyl undecanoate, coating efficiency 90.2 for undecanoate.

All columns were operated under isothermal conditions (190, 210 and 230 ºC). The carrier gas was nitrogen, the carrier gas flow 1 ml/min, injector temperature 250 ºC, split ratio 1:60, detector temperature 300 ºC, attenuation 1 and range 10^{-10} amps /mV.

The N-substituted amino *s*-triazines were synthesized from the corresponding amines using the general procedure of Thurston.[8] The purity of all products was controlled by GC, IR and NMR.

The hydrocarbons used in this study as standards were obtained from Fluka (Switzerland).

RESULTS AND DISCUSSION

Table I lists the parameters (*a*,*b*) of Eq. (1) and statistical data (*r*; correlation coefficient; *s*, standard error) for 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines on the capillary columns DB-1 and DB-5. Table II gives the parameters (*A*, *B*) of Eq. (2) and statistical data (*R*, correlation coefficient; *S*, standard error) for 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines on the same columns.

TABLE I. The parameters *a*,*b*; correlation coefficient *r* and standard error *s* for the linear regressions for Eq. (1) on capillary columns DB-1 and DB-5 in the temperature range 190–230 ºC (number of experimental points = 3) for 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines

Column	DB-1					DB-5				
Comp. No	*eI* 190 ºC	*b*	*a*	*r*	*s*	*eI* 190 ºC	*b*	*a*	*r*	*s*
1	1753.88	0.5957	1650.45	0.9972	1.25	1763.13	0.5957	1650.45	0.9972	1.26
2	1918.11	0.6650	1789.94	0.9730	4.45	1929.42	0.6652	1801.20	0.9732	4.44
3	2032.28	0.7212	1894.02	0.9894	2.98	2055.34	0.7217	1916.99	0.9896	2.96
4	2122.01	0.6175	2003.21	0.9794	3.60	2146.94	0.6185	2027.95	0.9794	3.60
5	2001.81	0.9735	1816.86	0.9999	0.15	2066.83	0.9740	1881.80	0.9999	0.08
6	2123.87	0.6970	1991.72	0.9991	0.81	2188.26	0.6980	2055.97	0.9991	0.82
7	2235.62	0.9012	2064.88	0.9988	1.22	2251.95	0.9013	2081.20	0.9988	1.22
8	1959.48	0.7702	1814.79	0.9829	4.07	2002.28	0.7710	1857.45	0.9829	4.07
9	2111.91	0.7772	1965.66	0.9875	3.49	2125.36	0.1800	1898.00	0.9955	3.20
10	2205.28	0.7417	2065.88	0.9841	3.77	2258.03	0.7420	2118.58	0.9843	3.75
11	2344.28	0.7400	2205.03	0.9877	3.30	2390.01	0.7400	2250.76	0.9876	3.32
12	1643.16	0.6900	1510.84	0.9902	2.74	1668.31	0.6912	1535.85	0.9903	2.73
13	1702.15	0.7232	1563.15	0.9825	3.87	1731.01	0.7237	1591.91	0.9825	3.87
14	1617.49	0.5047	1520.85	0.9922	1.79	1647.65	0.5055	1550.87	0.9922	1.78
15	1724.43	0.5167	1625.88	0.9982	0.87	1757.99	0.5175	1659.30	0.9989	0.85
16	1814.45	0.4607	1726.56	0.9979	0.84	1843.66	0.4615	1755.62	0.9978	0.84
17	1906.55	0.4772	1815.46	0.9972	1.00	1936.94	0.4770	1845.70	0.9972	1.00

TABLE II. The parameters *A*,*B*; correlation coefficient *R* and standard error *S* for the linear regressions for Eq. (2) on capillary columns DB-1 and DB-5 in the temperature range 190–230 ºC (number of experimental points = 3) for 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines

Column	DB-1					DB-5				
Comp. No	*eI* 190 ºC	*–B*	*A*	*R*	*S*	*eI* 190 ºC	*–B*	*A*	*R*	*S*
1	1753.88	138823	2053.95	0.9987	0.85	1763.13	138999	2063.58	0.9987	0.86
2	1918.11	154002	2248.70	0.9672	4.90	1929.42	154062	2260.15	0.9674	4.89
3	2032.28	167392	2392.34	0.9857	3.47	2055.34	167512	2415.66	0.9858	3.45
4	2122.01	143108	2429.42	0.9743	4.02	2146.94	143341	2454.85	0.9743	4.02
5	2001.81	226819	2491.34	0.9998	0.50	2066.83	226863	2556.43	0.9998	0.56
6	2123.87	162550	2474.97	0.9998	0.34	2188.26	162727	2539.74	0.9998	0.35
7	2235.62	210142	2689.58	0.9997	0.61	2251.95	210155	2705.94	0.9997	0.62
8	1959.48	180193	2349.92	0.9871	3.55	2002.28	180368	2393.10	0.9870	3.55
9	2111.91	181711	2505.41	0.9910	2.97	2125.36	276171	2720.80	0.9929	4.01
10	2205.28	173497	2581.16	0.9881	3.27	2258.03	173552	2634.02	0.9882	3.25
11	2344.28	172997	2518.90	0.9912	2.80	2391.01	173001	2764.64	0.9911	2.82
12	1643.16	160278	1987.96	0.9866	3.21	1668.31	160455	2013.50	0.9868	3.19
13	1702.15	167683	2062.49	0.9778	4.36	1731.01	167800	2091.60	0.9778	4.36
14	1617.49	117204	1869.71	0.9889	2.13	1647.65	117380	1900.25	0.9890	2.13
15	1724.43	120179	1983.43	0.9965	1.22	1757.99	120357	2017.38	0.9966	1.20
16	1814.45	107143	2045.33	0.9961	1.15	1843.66	107317	2074.91	0.9960	1.16
17	1906.55	110954	2145.59	0.9951	1.33	1936.94	111070	2176.23	0.9951	1.33

Table III lists the parameters of Eq. (1) and statistical data for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines on the capillary columns DB-1, DB-5 and DB-WAX. Table IV gives the parameters of Eq. (2) and statistical data for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines on the same capillary columns.

All experimental points were recorded in the temperature range 190–230 ºC (at 190, 210 and 230 ºC).

A rather good linear temperature dependence of the retention index is noticed for all used columns. Eq. (1), which is mostly used in the literature, shows a slightly better precision in comparison to Eq. (2) when 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines are considered, whereas Eq. (2) gives slightly better results than Eq. (1) for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines.

The standard error for some 2,4-bis(alkylamino)-6-chloro-*s*-triazines and 2-alkylamino-4,6-dichloro-*s*-triazines is around 1.00 or less. In most cases the standard error is higher indicating a hyperbolic curve. The *s*-triazines in this work were studied over a narrow temperature range of 40 ºC with only three experimental points. The hyperbolic temperature dependence of the retention index can be applied only for compounds having more experimental points.[9]

TABLE III. The parameters *a*, *b*; correlation coefficient *r* and standard error *s* for the linear regressions for Eq. (1) on capillary columns DB-1, DB-5 and DB-WAX in the temperature range 190–230 ºC (number of experimental points = 3) for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines.

Column	DB-1					DB-5					DB-WAX				
Comp. No.	*eI* 190ºC	*b*	*a*	*r*	*s*	*eI* 190 ºC	*b*	*a*	*r*	*s*	*eI* 190 ºC	*b*	*a*	*r*	*s*
18	2048.58	0.5540	1936.56	0.9801	3.17	2086.66	0.5967	1974.45	0.9865	2.88	2137.93	0.5947	2026.06	0.9864	2.79
19	2146.08	0.5300	2046.82	0.9732	3.53	2192.25	0.5475	2089.49	0.9804	3.11	2243.45	0.5472	2140.73	0.9805	3.09
20	2245.29	0.5585	2140.42	0.9818	3.05	2291.48	0.5757	2183.40	0.9808	3.23	2342.60	0.5787	2233.95	0.9811	3.22
21	2345.05	0.5645	2239.41	0.9705	3.96	2391.99	0.5525	2288.64	0.9687	4.00	2443.11	0.5545	2339.38	0.9698	4.00
22	2439.67	0.5602	2334.58	0.9786	3.32	2484.55	0.6100	2369.79	0.9871	2.79	2535.73	0.6112	2420.71	0.9876	2.74
23	2545.82	0.4672	2458.51	0.9646	3.61	2592.24	0.4807	2501.96	0.9818	2.62	2643.48	0.4800	2553.32	0.9827	2.55
24	2643.75	0.6225	2527.06	0.9763	3.89	2688.93	0.6447	2568.23	0.9748	4.42	2740.13	0.6442	2619.50	0.9723	4.37
25	2744.88	0.5560	2640.21	0.9887	2.37	2790.12	0.5912	2678.63	0.9923	2.07	2841.32	0.5912	2729.81	0.9926	2.03
26	2847.33	0.5160	2750.29	0.9860	2.46	2893.51	0.5145	2796.53	0.9915	1.91	2944.77	0.5127	2848.10	0.9919	1.84
27	2947.38	0.4800	2857.91	0.9544	4.24	2992.06	0.5270	2893.89	0.9518	4.80	3043.27	0.5267	2945.12	0.9526	4.75

TABLE IV. The parameters *A*, *B*; correlation coefficient *R* and standard error *S* for the linear regressions for Eq. (2) on capillary columns DB-1, DB-5 and DB-WAX in the temperature range 190–230 ºC (number of experimental points = 3) for 2,4-bis(cycloalkylamino)-6-chloro-*s*-triazines.

Column	DB-1					DB-5					DB-WAX				
Comp. No.	*eI* 190ºC	*–B*	*A*	*R*	*S*	*eI* 190 ºC	*–B*	*A*	*R*	*S*	*eI* 190 ºC	*–B*	*A*	*R*	*S*
18	2048.58	129709	2321.73	0.9846	2.79	2086.66	139551	2388.94	0.9894	2.48	2137.93	139068	2439.13	0.9901	2.39
19	2146.08	124133	2415.34	0.9785	3.17	2192.25	128125	2649.96	0.9848	2.73	2243.45	128065	2521.02	0.9849	2.73
20	2245.29	130676	2528.48	0.9860	2.67	2291.48	134730	2583.49	0.9851	2.84	2342.60	135425	2636.17	0.9855	2.83
21	2345.05	132252	2631.99	0.9761	3.57	2391.99	129465	2672.94	0.9744	3.62	2443.11	129931	2725.06	0.9745	3.62
22	2439.67	131137	2723.96	0.9832	2.94	2484.55	142619	2793.41	0.9906	2.37	2535.73	142901	2845.18	0.9911	2.33
23	2545.82	109534	2783.61	0.9706	3.30	2592.24	112484	2836.00	0.9861	2.29	2643.48	112295	2886.81	0.9868	2.23
24	2643.75	145747	2959.80	0.9812	3.47	2688.93	151033	3016.58	0.9772	3.98	2740.13	150907	3067.50	0.9777	3.93
25	2744.88	129960	3026.26	0.9921	2.00	2790.12	138111	3088.98	0.9950	1.68	2841.32	138103	3140.14	0.9953	1.64
26	2847.33	120662	3108.68	0.9897	2.12	2893.51	120203	3153.65	0.9943	1.56	2944.77	119784	3203.98	0.9947	1.50
27	2947.38	112628	3192.09	0.9613	3.92	2992.06	123683	3260.85	0.9588	4.44	3043.27	123616	3311.89	0.9596	4.40

CONCLUSION

The linear temperature dependence of retention index for *s*-triazines was established on capillary columns of different polarity. A good linearity of the retention index versus column temperature was found in the investigated temperature range.

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ИЗВОД

ГАСНОХРОМАТОГРАФСКИ РЕТЕНЦИОНИ ИНДЕКСИ N-СУПСТИТУИСАНИХ АМИНО ДЕРИВАТА *s*-ТРИАЗИНА НА КАПИЛАРНИМ КОЛОНАМА. ДЕО V. УТИЦАЈ ТЕМПЕРАТУРЕ НА РЕТЕНЦИОНИ ИНДЕКС

ДУШАН Ж. МИЈИН, ДУШАН Г. АНТОНОВИЋ и БРАТИСЛАВ Ж. ЈОВАНОВИЋ

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У раду је приказана линеарна заивсност ретенционог индекса од температуре коришћењем линеарних зависности ретенционог индекса у функцији температуре колоне t, °C или $1/T$, K^{-1} за *s*-триазине на капиларним колонама DB-1, DB-5 и DB-WAX у температурном интервалу 190–230 °C.

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REFERENCES

1. K. Heberger, M. Gorgenyi, T. Kowalska, *J. Chromatography A* **973** (2002) 135
2. E. Tudor, *J. Chromatography A* **779** (1997) 287
3. E. Tudor, *Rev. Roumain. Chim.* **43** (1998) 587
4. D. G. Antonović, G. A. Bončić, *J. Serb. Chem. Soc.* **59** (1994) 993
5. D. G. Antonović, G. A. Bončić, *J. Serb. Chem. Soc.* **60** (1995) 669
6. O. S. Rajković, D. G. Antonović, B. Ž. Jovanović, G. A. Bončić, *J. Serb. Chem. Soc.* **59** (1996) 993
7. D. Ž. Mijin, D. G. Antonović, G. A. Bončić, B. Ž. Jovanović, O. S. Rajković, *J. Serb. Chem. Soc.* **68** (2003) 557
8. J. T. Thurston, J. R. Dudley, D. W. Kaisler, J. Hechenbleinker, F. C. Shafner, D. Holm-Hansen, *J. Am. Chem. Soc.* **73** (1951) 2983
9. E. Tudor, *J. Chromatography A* **848** (1999) 215.