*J.Serb.Chem.Soc.* 68(7)557–564(2003)
*JSCS – 3073*

UDC 547–304.9:543.544.3:66–948.3
*Original scientific paper*

# Gas chromatograpic retention indices for N-substituted amino *s*-triazines on capillary columns. Part IV. Influence of column polarity on retention index

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(Received 29 July, revised 26 November 2002)

*Abstract*: The retention index increment for the addition of a methylene group to the alkyl group of an analyte molecule is shown to be lower than 100 i.u. for N-substituted amino *s*-triazines. In temperature progammed gas chromatography, a linearly interpolated retention index *I*, determined from the linear regression equation, $I = AZ + (GRF)_z$, with the number of atoms (*Z*) in the molecule as variable, was used to describe the retention of 25 N-substituted amino *s*-triazines, on DB-1, DB-5 and DB-WAX capillary columns, divided into five series according to the similarity of the alkyl groups in the particular series. In the above equation, *A* is the linear regression coefficient or the retention index increment per atom addition, *Z* the number of C, N and Cl atoms in the molecule, and $(GRF)_z$ the group retention factor or functionality constant for functional groups in the molecule, based on the number *Z*. It is possible to estimate the retention indices of an unknown member of the series from the *Z*, *A* and (*GRF*) values.

*Keywords*: retention indices, retention index increment, *s*-triazines, group retention factors.

## INTRODUCTION

One of the most powerful tools in analytical chemistry is without doubt gas chromatography. Unsurpassed as a separation technique, it produces one single value for each analyte, which may be used for identification purposes. Gas chromatographic retention is a very complex process since it involves the interaction of a multitude of intermolecular forces such as London or dispersion forces, Keesom or dipole–dipole forces, Debye or dipole-induced dipole forces and electron donor–acceptor complexation, including hydrogen bonding forces. Other factors, such as adsorption at the gas–liquid and liquid–support interfaces, steric hidrance of substituent groups within the solution molecule, *etc.*, also affect the retention.[1,2]

An early observation by James and Martin[3] was the fact that a plot of the logarithms of the corrected retention volumes of members of a homologous series *versus* their carbon

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number was a straight line when homologues of at least five or six carbon atoms were considered. A straight line may be clearly observed if the logarithms of the adjusted retention times are plotted *versus* the carbon number. Based on this idea, Kovats[4] proposed increasing the number of reference substrances by presenting his retention index system. In the Kovats retention index system *n*-alkanes are the retention index markers. Their *I* values are arbitrarily assigned to equal the number of carbon atoms (*n*) in the molecule multiplied by 100,[1,5] thus:

$$I = 100n \tag{1}$$

The Kovats retention index system uses logarithmic interpolation for calculation of the isothermal retention index of an analyte molecule bracked by the retention times of two adjacent *n*-alkanes, while the temperature-programmed retention index system uses linear interpolation. In temperature-programmed chromatographic system, Eq. (1) can be derived from an equation that equates the retention index to the summation of atom and functionality contribution of the analyte molecule,[2] thus:

$$I = AZ + (GRF)_z \tag{2}$$

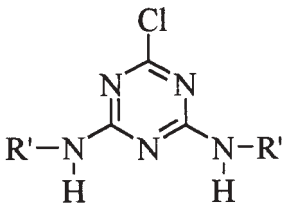
where *A* is the linear regression coefficient or the retention index increment per atom addition, *Z* the number of C, N and Cl atoms in the molecule, and $(GRF)_z$ the group retention factor or functionality constant of the functional groups in the molecule, based on the number *Z*. Equation (2) is reduced to Eq. (1) for *n*-alkanes, by seting the term (*GRF*) to zero because of the absence of functionality in the molecule, and *A* is arbitrarily assigned a value of 100 index units (i.u.).

As a part of our study[6–8] of chemical structure-retention index relationships, we report here a study of the retention of a series of 25 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), 4 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)-Cl-*s*-triazine (di-*N*-substituted cycloalkylamino derivatives of *s*-triazines) (Fig. 1) on capillary columns of different polaryti (DB–1, DB–5 and DB–WAX). For eaisier discussion, the alkylamino derivatives of *s*-triazines are divided into series as given in Fig. 1.

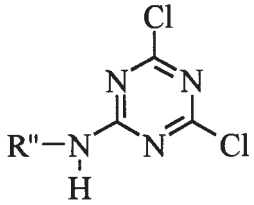
## EXPERIMENTAL

The GC analyses were performed on a Varian 3400 gas chromatograph equipped with a flame ionization detector and an glass split-splitless sample injector (1071 capillary injector). Data handling was provided by a Varian 4720 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 n-undecanoate, coating efficiency 90.2 for *n*-undecanoate).



(I)



(II)

where R' is:

*Ser 1.*
1-Methylethyl (1),
Methylpropyl (2),
1,2-Dimethylpropyl (3),
1,2,2-Trimethylpropyl (4),
*Ser. 2*
1-Methylpropyl (2),
1-Methylbutyl (5),
1,3-Dimethylbutyl (6),
1,3,3-Trimethylbutyl (7),
*Ser 3.*
1,1-Dimethylpropyl (8),
1,1-Dimethylbutyl (9),
1,1,3-Trimethylbutyl (10),
1,1,3,3- Tetramethylbutyl (11),
*Ser. 5.*
Cyclopropyl (16)
Cyclobutyl (17),
Cyclopentyl (18),
Cyclohexyl (19),
Cycloheptyl (20),
Cyclooctyl (21),
Cyclononyl (22),
Cyclodecyl (23),
Cycloundecyl (24),
Cyclododecyl (25)

and R" is:

Ser. 4.
1,1-Dimethylpropyl (12),
1,1-Dimethylbutyl (13),
1,1,3-Trimethylbutyl (14),
1,1,3,3-Tetramethylbutyl (15)

Fig. 1. Structural formula of the studied 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).

The temperature program used was as follows: initial column temperature 60 ºC, initial hold time 10.0 min, final column temperature 244 ºC, heating rate 4 º/C and final column hold time 10.0 min.

The N-substituted amino *s*-triazines were synthesized from the corresponding amines using the general procedure of Thurston.[9] The purity of all products was controled by GC, IR and NMR.

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

The carrier gas was nitrogen (flow rate 1 ml/min), injector temperature 250 ºC, split ratio 1:60, detector temperature 300 ºC, attenuation 1 and range $10^{-10}$ A/mV.

## RESULTS AND DISCUSSION

In this study, the gas chromatographic retention indices (*I*) of 25 N-substituted amino derivatives of *s*-triazines obtained on DB-1, DB-5 and DB-WAX capillary columns using programmed temperature gas chromatography (TPGC) were used to show that the retention in a temperature-programmed chromatographic system is a simple function of the number of atoms (*Z*) even if in the series of compounds the next member is more hindered by branching or increasing of the size of the ring present in the molecule. Specifically, in most of the studied N-substituted amino derivatives of *s*-triazines, the next member in the series was obtained by the addition of two methylene groups (Fig. 1, formula I), which increases the voluminosity of the molecule.

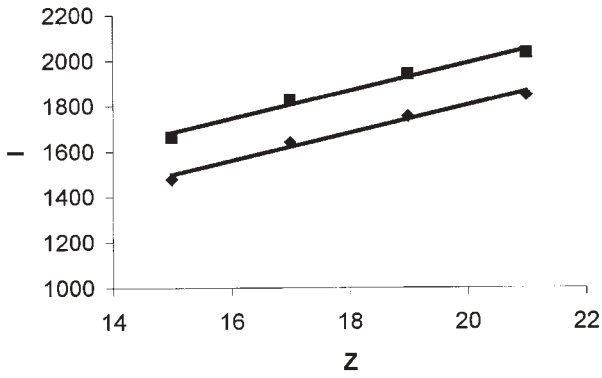



Fig. 2. Linear plots of *I vs. Z* of the *s*-triazines of the series 1 on DB-1 (◆) and DB-5 (■) columns.

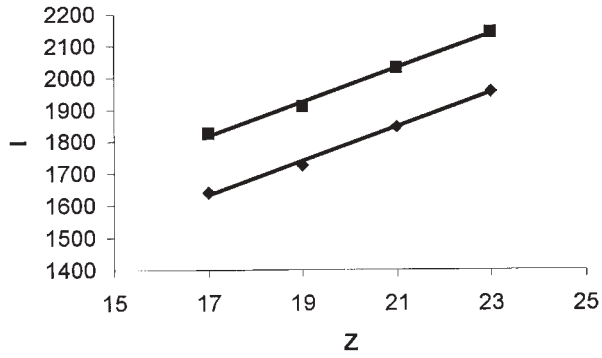



Fig. 3. Linear plots of *I vs. Z* of the *s*-triazines of the series 2 on DB-1 (◆) and DB-5 (■) columns.

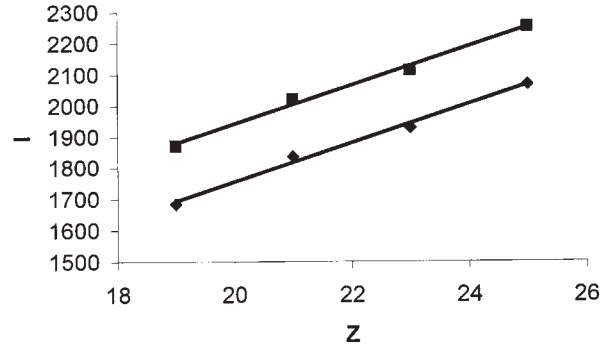



Fig. 4. Linear plots of *I vs. Z* of the *s*-triazines of the series 3 on DB-1 (◆) and DB-5 (■) columns.

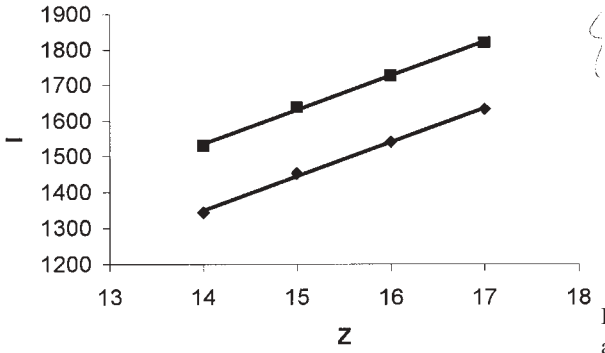



Fig. 5. Linear plots of *I vs. Z* of the *s*-triazines of the series 4 on DB-1 (◆) and DB-5 (■) columns.

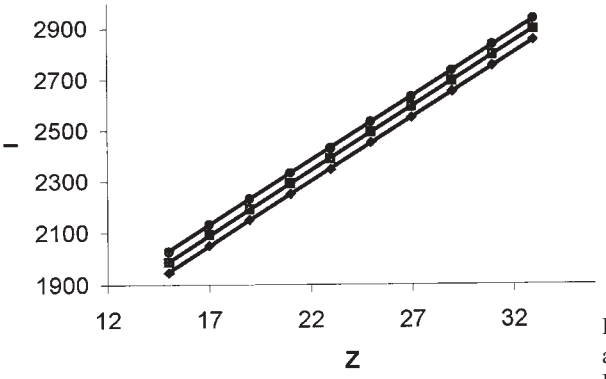



Fig. 6. Linear plots of *I vs. Z* of the *s*-triazines of the series 5 on DB-1 (◆) and DB-WAX (●) columns.

Linear plots of the gas chromatographic retention indices (*I*) *vs. Z* of the N-substituted amino derivatives of *s*-triazines are shown in Figs. 2–6. The gas chromatographic retention indices (*I*) and the number of atoms *Z*, where *Z* is the number of C, N, Cl atoms in the molecule, were used for linear regression analyses. The *A* and (*GRF*) values for each series of N-substituted amino derivatives of *s*-traizines are given in Table I together with the number of points (*n*) used for the linear regression. The quality of the fit, as measured by the correlation coefficient (*R*), is also given.

The conventional procedure of predicting the retention index of an analyte molecule is to calculate the base value of the molecule by assuming the *A* value of each atom in the molecule is 100 i.u. (*i.e.*, $AZ = 100\ Z$) of retention index and then add to it the interaction or functionality contribution, *i.e.*, the (*GRF*) value, according to Eq. (2). In the study of the N-substituted amino derivatives of *s*-triazines that is not the case in any of the series. The closest to the 100 value is series 4 ($A = 95.59$–$95.79$), in which only one methylene group is added to the alkyl group to obtain next member in the series. The reason for the deviation from 100 is probably caused by the presence of Cl and N atoms in the molecule, as well as

by branching in the series, which on the other hand influence the interaction between the molecule and the column.

TABLE I. Linear regression coefficients (*A*) and intercepts (*GRF*) for the 25 *N*-substituted amino *s*-triaziens, on DB-1, DB-5 and DB-WAX capillary columns, divided into five series according to the similarity of the alkyl groups in the certain series, and the number of data points (*n*) used for linear regression analyssis and correaltion coefficient of the fit (*R*)

| Series | Column | | |
|---|---|---|---|
| | DB-1 | DB-5 | DB-WAX |
| *Ser. 1.* | | | |
| *A* | 61.07 | 61.20 | |
| $(GRF)_z$ | 579.94 | 762.98 | |
| *n* | 4 | 4 | |
| *R* | 0.9917 | 0.9919 | |
| *Ser. 2.* | | | |
| *A* | 53.49 | 53.49 | |
| $(GRF)_z$ | 721.51 | 906.43 | |
| *n* | 4 | 4 | |
| *R* | 0.9977 | 0.9977 | |
| *Ser. 3.* | | | |
| *A* | 62.15 | 62.10 | |
| $(GRF)_z$ | 511.20 | 697.69 | |
| *n* | 4 | 4 | |
| *R* | 0.9961 | 0.9961 | |
| *Ser. 4.* | | | |
| *A* | 95.59 | 95.79 | |
| $(GRF)_z$ | 10.48 | 193.79 | |
| *n* | 4 | 4 | |
| *R* | 0.9990 | 0.9990 | |
| *Ser. 5.* | | | |
| *A* | 50.22 | 50.26 | 50.22 |
| $(GRF)_z$ | 1193.63 | 1234.69 | 1275.60 |
| *n* | 10 | 10 | 10 |
| *R* | 0.9999 | 0.9999 | 0.9999 |

Concerning the other series, *A* is much smaller than 100. Firstly, in these series, the series grow by the addition of two mehylene groups, since there are two alkyl groups present in the molecule of *s*-triazines. In series 1, 2 and 3, the alkyl groups are highly branched, while in series 5, cycloalkyl groups grow. One atom of Cl, however, remains in each *s*-triazine. Such molecular structures of the *s*-triazines significantly change their interaction with the column thus giving rise to much lower *A* values.

A value of *A* smaller than 100 i.u. is interpreted to mean that the electron density distribution in the molecule is such as to allow the backbone structure of the analyte molecule to be retained for shorter times than the corresponding *n*-alkane molecule. In other words, a value of *A* lower than 100 indicates a lower electron density in the backbone structure of the analyte molecule than that of the corresponding *n*-alkane; the analyte molecule will be retained for a shorter period.

The retention indices of all five series of *s*-triazines on all capillary columns obey the retention index equation, Eq. (2), with very high correlation coefficinets (from 0.9961 to 0.9999). Both the *A* and (*GRF*) values are characteristic of the series and the strationary liquid phase. The *A* values for DB-1, DB-5 and DB-WAX columns for the studies *s*-triazines are almost the same while the (*GRF*) values increase with the polarity of stationary liquid phase (DB-1 < DB-5 < DB-WAX). In general, the *A* and (*GRF*) values represent different aspects of intermolecular interaction between the analyte and the stationary liquid phase. The *A* value is particularly affected by dipole–dipole interactions and the (*GRF*) value by H-bonding in the intermolecular interactions.

The DB-1 column is the most non-polar liquid phase and contains only Si–O and Si–C linkages with no polarizible or polar side chains and with only a minimum capability and polarity for intermolecular interactions with the analyte molecule. The backbone of the polyethylene glycol polymer on the DB-WAX column contains a string (C–C–O) groups which interact by hydrogen bonding with the analyte molecule to contribute to longer retention times. For this reason, the (*GRF*) value of series 5 is the highest on the DB-WAX column. On the other hand, the (*GRF*) values are the lowest on the DB-1 column. Since the *A* values are almost the same on each column, there is no change in dipole–dipole interactions between the analyte molecule and the polymeric stationary liquid phase. In this case ($A_1 = A_2$), the difference between two *I* values ($\Delta I$, the column difference, Eq. (3)) of the same compound on two columns of different polarities is equal to the difference in the (*GRF*) values (Eq. (4)).[2,5]

$$\Delta I = I_{\text{more polar}} - I_{\text{less polar}} = I_1 - I_2 = \\ = \{A_1 Z + (GRF)_1\} - \{A_2 Z + (GRF)_2\} \quad (3)$$

$$\Delta I = (GRF)_1 - (GRF)_2 \quad (4)$$

According to Eq. (2), the values of *Z*, (*GRF*) and *A* determine the retention of an analyte molecule.[2] Using the obtained data from this work, the retention index of the studied *s*-triazine can be predicted if all three values are given. Or, the eluation sequence can be predicted if only two of the values are known.

*Acknowledgment*: The authors are grateful to the Ministry of Science Technologies and Development of Serbia for financial support (Project No. 1694).

ИЗВОД

# ГАСНО ХРОМАТОГРАФСКИ РЕТЕНЦИОНИ ИНДЕКСИ N-СУПСТИТУИСАНИХ АМИНО ДЕРИВАТА *s*-ТРИАЗИНА НА КАПИЛАРНИМ КОЛОНАМА. ДЕО IV. УТИЦАЈ ПОЛАРНОСТИ КОЛОНЕ НА РЕТЕНЦИОНИ ИНДЕКС

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У температурно-програмираном хроматографском систему, промена ретенционог индекса (*I*) се може приказати као функција збира удела атома и функционалних група анализираног молекула, тј. $I = AZ + (GRF)_Z$, при чему *A* представља линеарни регресиони коефицијент или прираштај ретенционог индекса по збиру атома (d*I*/d*Z*), *Z* број атома угљеника, азота и хлора у молекулу *s*-триазина, $(GRF)_z$ ретенциони фактор групе или функционалну константу функционалних група у молекулу, базирану на броју атома, *Z*. У раду је приказана линеарна зависност ретенционог индекса, добијеног коришћењем температурно програмиране гасне хроматографије, у функцији броја атома угљеника, азота и хлора код 25 деривата *s*-триазина. Посматрани деривати *s*-триазина су подељени у пет серија према структурној сличности и одређене су вредности *A* и (*GRF*) за сваку серију. Најбоља корелација је добијена код *N*-циклоалкил деривата *s*-триазина.

(Примљено 29. јула, ревидирано 26. новембра 2002)

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