https://doi.org/10.3311/PPch.37088

Periodica Polytechnica Chemical Engineering, 68(4), pp. 630–638, 2024

Comparison of 624-type Capillary Columns II

"Equivalent Columns" Deviation in the Quantitative Analysis

Judit Mátyási[1,2*], Gyula Nyerges[1], József Balla[1,2]

[1] Department of Inorganic and Analytical Chemistry, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[2] B&B Analytics Ltd., Terasz u. 60., H-2030 Érd, Hungary
[*] Corresponding author, e-mail: matyasi.judit@vbk.bme.hu

Received: 09 April 2024, Accepted: 15 August 2024, Published online: 27 August 2024

Abstract

The present paper is the continuation of our "equivalent column" study. 624-type columns were investigated in a capillary gas chromatograph with a flame ionization detector (FID). In the preceding work, we used a homemade test mixture containing mainly acidic type compounds, which we complemented in the current study with additional basic test compounds to give a more precise description of the behaviour of the stationary phases. The columns had the same dimensions (30 m × 0.32 mm × 1.0 μm; length, internal diameter and film thickness, respectively) but were purchased from different manufacturers or the same manufacturer but from different batches. In addition, also their pre-life was different. These circumstances influence the condition of the stationary phase, and therefore their separation ability. These factors imply the necessity of testing the column from time to time. To distinguish between the separation ability of the columns, we compared the chromatograms, the retention times and retention order of the molecules, as well as peak asymmetry factors. Besides these parameters, quantitative determination is also performed based on the results of separation. We used the effective carbon number (*ECN*) and the limit of quantitation (*LoQ*) to demonstrate these differences which are caused by the different stationary phase conditions.

Keywords

column test, 624 capillary column, effective carbon number, limit of quantitation

1 Introduction

With quantitative gas chromatography measurements, the primary objective is to provide the necessary resolution and limit of quantitation (*LoQ*). After selecting the theoretically appropriate stationary phase for separation, analysts should decide whether to choose one from the laboratory column stock on hand or purchase a brand-new one from one of the manufacturers present on the market. Not only the history of a column but also different manufacturing technologies can affect the desirable results. In the case of a used column, the history of the column needs also be reckoned with. The stationary phase preserves the imprint of the previously measured samples in the form of irreversibly bonded contaminations. These inevitably lead to an alteration in its quality. When buying a new column, differences may be expected due to different manufacturing technologies. The manufacturers provide a test chromatogram and the calculated chromatographic parameters such as selectivity, resolution, peak asymmetry factor, or height equivalent to a theoretical plate for some chosen compounds. However, the test mixture and the chromatographic circumstances could differ from producer to producer, which makes it difficult to compare the "equivalent columns". Even if the parameters are similar, sometimes it is difficult to tell the differences. In order to find the proper column for the analysis at hand, the analyst should test their columns with their specific test mixture in similar conditions [1].

By introducing the retention index system in 1958, Kováts [2] laid the foundations for the classification system of gas chromatographic stationary phases. This system was used by Rohrschneider [3], who chose five different test molecules to represent the second-order interactions between the analyte and the stationary phase. He determined the retention indices of the test molecules on 20 stationary phases and compared them to the indices measured on squalane chosen as reference. McReynolds [4]

Cite this article as: Mátyási, J., Nyerges, G., Balla, J. "Comparison of 624-type Capillary Columns II: "Equivalent Columns" Deviation in the Quantitative Analysis", Periodica Polytechnica Chemical Engineering, 68(4), pp. 630–638, 2024. https://doi.org/10.3311/PPch.37088

extended this method to a wider stationary phase range by changing the test compounds (gaseous alkanes were eliminated). For some cases, he suggested other five compounds for a more accurate determination of the average polarity of the phases. As the 0 value of the chromatographic polarity index scale, squalane (most apolar), and for the 100 value, 100% cyanopropyl siloxane was chosen. Using the McReynolds data with a pattern cognition method, Wold [5] classified 198 of 226 stationary phases into 16 clusters and distinguished 28 unique phases. In addition to the classification based on the retention index, grouping as per thermodynamic parameters such as sorption enthalpy is also widely used. Poole et al. [6] found that, on polar phases, the calculated selectivity based on the retention index is ridden with error due to the different dissolution mechanisms of the alkanes. By using the partial molar Gibbs free energy of solution for a homologue series of solutes they determined the polarity index based on the free energy of solvation of the methylene increment $\left(\Delta G_s^0\left(CH_2\right)\right)$. Abraham et al. [7] established a solvation equation between the retention volume and the different types of interactions with the stationary phase and calculated $\Delta G_s^0\left(CH_2\right)$ for 77 phases. The classification of the phases is consistent with Wold's clusters [5]. In 2000, this linear solvation energy model was corrected and revised, however, the results were found to be similar [8].

These classification methods led to distinguishing the stationary phases based on polarity. However, not only polarity but also selectivity affects the results. In 1978, Grob et al. [9] introduced a 12-component test mixture to model all possible gas chromatographic interactions between analytes and stationary phases. The method required only one single injection to evaluate the information about the state of the stationary phase. Based on this technique it became possible to compile a database, which groups similar phases according to the chromatogram pattern observed. Three years later, they [10] complemented these results with new experiences and recommendations for the analysis. Although this is a single injection testing method, in some cases it is complicated to set the measurement conditions as per the length of the column or the quality of the carrier gas. In other cases, even the test mixture is not suitable for testing unique stationary phases.

In the literature, other test mixtures with different compositions can also be found. Horká et al. [11] tested a mixed Carbowax 20M and SE-54 phase with volatile fatty acids and amines, and calculated column efficiency and capacity factor with 2,6-dimethylaniline and 2,6-dimethylphenol. Dresen et al. [12] applied only compounds containing nitrogen to test the performance of base-deactivated columns. Mehran et al. [13] carried out their column tests with alkyl halogenides, alkanes, toluene, and 2-methyl-1-butanol to compare different stationary phases based on the elution order and the calculated sorption enthalpies and entropies.

In our previous studies [14, 15] we investigated polyethylene glycol and 5% diphenyl – 95% dimethyl polysiloxane stationary phase gas chromatographic columns produced by different manufacturers. We modified the Grob test mixture to the isothermal measurement conditions to provide enough retention and avoid co-elutions. We demonstrated that the chromatogram of the test mixture on "equivalent columns" shows deviations. We determined sorption enthalpies and entropies to present the strength of the interactions between the different types of analytes and the stationary phase. We calculated the height equivalent to a theoretical plate (HETP) at 8 linear velocity (u) levels. With HETP – u curves, we visualized the deviations in the efficiency change of the columns to be compared.

The 624-type columns contain 6% cyanopropylphenyl – 94% dimethylpolysiloxane stationary phase which is commonly used for volatile compounds separation. This phase has strong dipole and hydrogen-bond base interactions, although the interactions with the analytes' lone electron pair are weak [16]. Becerra et al. [17] compared the OV-101 (dimethyl polysiloxane) and OV-105 (5% cyanopropyl – 95% dimethyl polysiloxane) stationary phases using the specific retention volumes, solute-polymer interaction parameters, and the partial molar enthalpies of solution and mixing. They found that the increasing cyanopropyl content of the stationary phase decreased the contribution of the methylene group to the partial molar free energy of the n-alkanes solution and increased the polarity of the phase. Fernández-Sánchez et al. [18] established, using Kováts' coefficient, that the polarity of the dimethyl polysiloxane stationary phase increases by increasing the ratio of the phenyl and/or cyanopropyl groups. Kiridena et al. [19] investigated the difference between the DB-608 (50% diphenyl – 50% dimethyl polysiloxane) and DB-624 columns using the solvation parameter model. They also confirmed the equivalent selectivity of the DB-624 and DB-1301 columns by the regression of the retention factors of a wide range of test compounds. Caulfield et al. [20] compared the strength of interactions between nitroaromatic explosives and 4 different stationary phases. Based on the calculated enthalpy of the solution, the strength of the interactions in the following order was established. The weakest interactions were formed with the 20% diphenyl – 80% dimethyl polysiloxane, which was followed by 14% cyanopropylphenyl – 86% dimethyl polysiloxane, then 50% diphenyl – 50% dimethyl polysiloxane, and finally polyethylene glycol phase.

In the FID, due to the hydrogen flame burning, a complex pool of radicals, ions and electrons is formed. The charged particles resulting from the radical mechanism chain reaction are set in motion by two electrodes between which there is a potential difference of 150–300 V. As a result of this movement the electrical circuit closes and the generated electrical signal is measurable as current or voltage. If only detector gases (hydrogen, air, and nitrogen) enter the flame only a low electrical current is generated, however, in the case of carbon-containing compounds it increases by orders of magnitude. For hydrocarbons, the signal is proportional to the carbon content of the molecule. This results from the formation of the ground state CH radicals and the proportionally generated electrons to them. [21]. However, heteroatom-containing molecules break this proportionality. Atoms, other than carbon and hydrogen, modify the signal depending on their quality and the type of the functional group in which they take place [21, 22]. Data are found in the literature for the different effects on the FID response specific to functional groups [22–26].

Sternberg [22] used Eq. (1) to define the effective carbon number (*ECN*) to describe the detector responses of the heteroatom-containing molecules:

$$ECN_i = n_s \times \frac{A_i \times m_s \times M_i}{A_s \times m_i \times M_s} = n_s \times f_i \times \frac{M_i}{M_s}, \qquad (1)$$

where *s* index is for the standard molecule, *i* is the index for the investigated molecule, *n* is the carbon number, *A* is the area of the peak, *m* is the mass of the molecule, *M* is its molar mass and *f* is the relative response.

Although the different molecule classes have their own characteristic effective carbon number increments, as we earlier demonstrated, the various chromatographic parameters have an effect on *ECN* [27, 28].

In this study, we complement our latest results [1] on seven 624-type gas chromatographic columns. The selected test compounds were split into two test mixtures based on their characteristics and also their retention to avoid overlapping. In the previous study, we investigated mainly oxygenated (aldehyde, alcohol, acid, ester) compounds, furthermore chloroalkane, an aromatic hydrocarbon and some nitrogen-containing molecules (amide, sulphonamide). However, in the present study, we complemented the test substances with aromatic and aliphatic ethers, a diol and a polycyclic compound and a nitroaromatic, as well as a heterocyclic compound and amines to receive a more basic test mixture.

The pattern of the chromatogram provides us with an opportunity to compare the equivalent stationary phases from different manufacturers and/or with different histories. The strength of the reversible interactions with the stationary phases can be illustrated with the peak asymmetry factor. The irreversible interactions are manifested as decreased peak areas. These differences are visualized with the calculated *ECN* and limit of detection. Our column test method described in the previous and present paper, is capable of indicating even the little differences that can be critical during method development and method adaptation.

2 Experimental

2.1 Reagents

The 8 selected test compounds are shown in Table 1 [22–25, 29]. As references n-heptane, n-nonane, n-undecane and n-tridecane were used.

The standards were purchased from Sigma-Aldrich. 25 mg of each compound was measured into a 25 mL volumetric flask and diluted with methanol. 1 mL of the stock solution was diluted to 20 ml with methanol. The concentration of the test molecules was approximately 50 µg mL^{-1}.

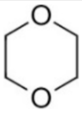
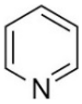
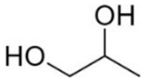
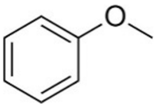
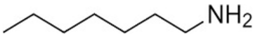
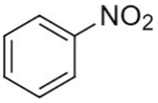
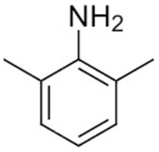
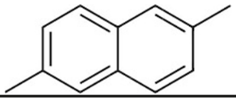
All the test compounds can form dispersion interactions with the stationary phase. Except for the 2,6-dimethylnaphthalene, all molecules can form dipole-dipole interactions. *π-π* interactions can be modelled with pyridine, anisole, nitrobenzene, 2,6-dimethylaniline, and 2,6-dimethylnaphthalene. Pyridine, heptylamine, and 2,6-dimethylaniline represent basic characteristics. 1,2-Propanediol is an electron pair acceptor, while the other molecules except 2,6-dimethylnaphthalene are electron pair donors.

2.2 Columns

We tested the same seven 624-type columns that were investigated in our previous paper (Table 2); however, with a different test solution containing a larger number of basic compounds than acidic ones.

The columns' dimensions were 30 m × 0.32 mm × 1.0 µm. The columns, supplied by the same manufacturer but coming from different batches, were marked with "a" and "b" to be distinguished. All columns were used for different samples. Before testing conditioning was applied in every case.

Table 1 Test compounds

No.	Name	Theoretical *ECN*	Structure
2	1,4-Dioxane	2[1]	
3	Pyridine	4.26[2]	
4	1,2-Propanediol	1.65[1]	
6	Anisole	6.14[2]	
7	Heptylamine	6.11[3]	
9	Nitrobenzene	≤ 6	
10	2,6-Dimethyl-aniline	7.5[4]	
12	2,6-Dimethyl-naphtalene	11.95[5]	

[1] Sternberg et al. [22]; [2] Jorgensen et al. [23]; [3] Kállai et al. [24]; [4] Kállai et al. [25]; [5] Scanlon et al. [29]

Table 2 The tested columns

No.	Column	Manufacturer
1	Rtx-624 a	Restek
2	Rtx-624 b	Restek
3	CP Select 624 a	Agilent
4	CP Select 624 b	Agilent
5	DB-624	Agilent
6	ZB-624	Phenomenex
7	Elite-Volatiles	Perkin Elmer

2.3 Apparatus

A Shimadzu GC-2014 gas chromatograph was applied with an AOC-20i autosampler. The injector was held at 250 °C, and 1 μL test solution was injected at each measurement condition five times. To prevent excess sorption in the injection port, liners were silylated before use. The test solution was measured at 50, 100, 150, and 200 cm s^{-1} linear velocity. Hydrogen (purity 99.98%) was applied as a carrier gas. The split ratio was 20:1. The column temperature program started at 40 °C, then programmed to 220 °C at a rate of 5 °C min^{-1}. The flame ionization detector was held at 250 °C. The hydrogen, air, and nitrogen (make-up, purity 99.996%) gas pressures applied in the FID were 75 kPa, 50 kPa, and 60 kPa, respectively.

2.4 Effective carbon number

The theoretical *ECN* values of the target compounds are listed in Table 1. These values are based on our earlier and other authors' *ECN* studies. In case no experimentally determined *ECN* was available for the specific compounds, we indicated a calculated value based on the sum of the *ECN* increments characteristic for the molecule functional groups. No data was found in the literature for the $–NO_2$ group.

3 Results and discussion

3.1 Retention order

Chromatograms evaluated on the tested columns are shown in Fig. 1. Except for the Elite Volatiles column, the retention order was the same for every column. Although the Elite Volatiles column is listed as a 624 column in the cross-reference lists, it has a slightly different stationary phase. The apolar alkanes had similar retention times on every column, but the polar test compounds had less retention on the Elite-Volatiles. This means that this stationary phase is less polar than the 624 columns. The retention order of pyridine (3) and 1,2-propanediol (4) changed on Elite-Volatiles to 1,2-propanediol (4) and pyridine (3), In addition, n-undecane (8) co-eluted at 50 cm s^{-1} with nitrobenzene (9).

Although as on every column, the peak maximum of heptylamine appeared between anisole and n-undecane on the Rtx-624 b column, its retention time was significantly higher, and eluted partially under the n-undecanone. However, this retention time increase was not observed on the other Rtx-624 column (Rtx-624 a).

3.2 Peak shape

The asymmetry factor (A_s) was used to describe the peak distortion due to the stronger interaction between the stationary phase and the test molecules (Fig. 2). These values were calculated with Eq. (2):

$$A_s = \frac{b}{a}, \tag{2}$$

where b is the distance between the peak maximum and the endpoint of the peak at 10% peak height, and a is the distance between the start point and the maximum of the peak at 10% peak height. The maximum point is the retention time of the compound. The results show that almost all peaks have tailing (Fig. 3 (a)). However, significant

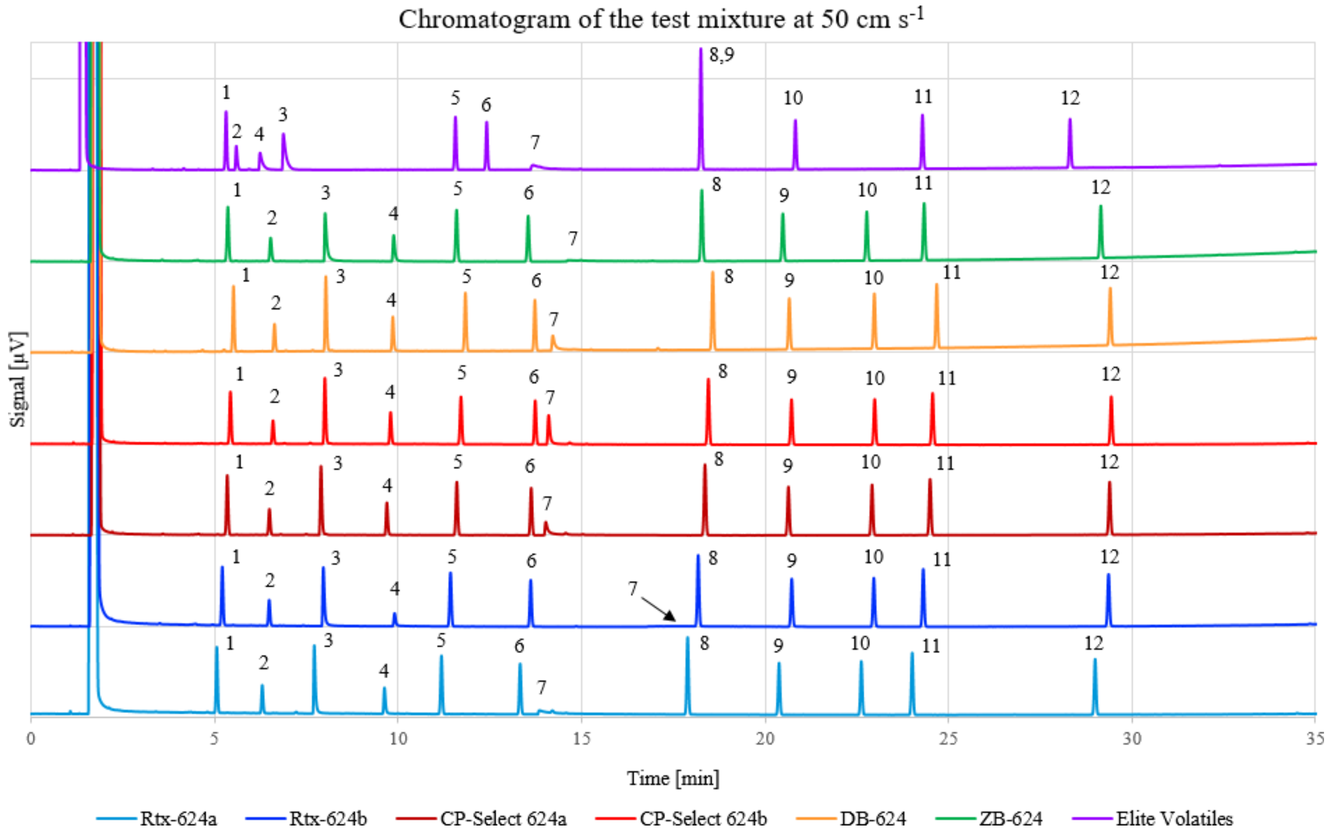


Fig. 1 Chromatogram of the test mixture on the investigated columns. Assignation of the peaks:
1 – n-Heptane, 2 – 1,4-Dioxane, 3 – Pyridine, 4 – 1,2-Propanediol, 5 – n-Nonane, 6 – Anisole, 7 – Heptylamine, 8 – n-Undecane,9 – Nitrobenzene, 10 – 2,6-Dimethylaniline, 11 – n-Tridecane, 12 – 2,6-Dimethylnaphtalene

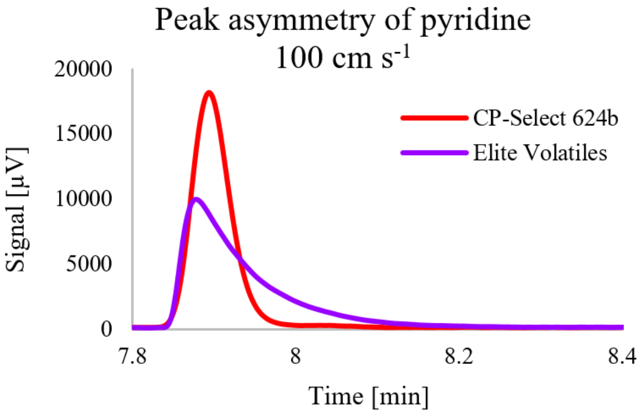


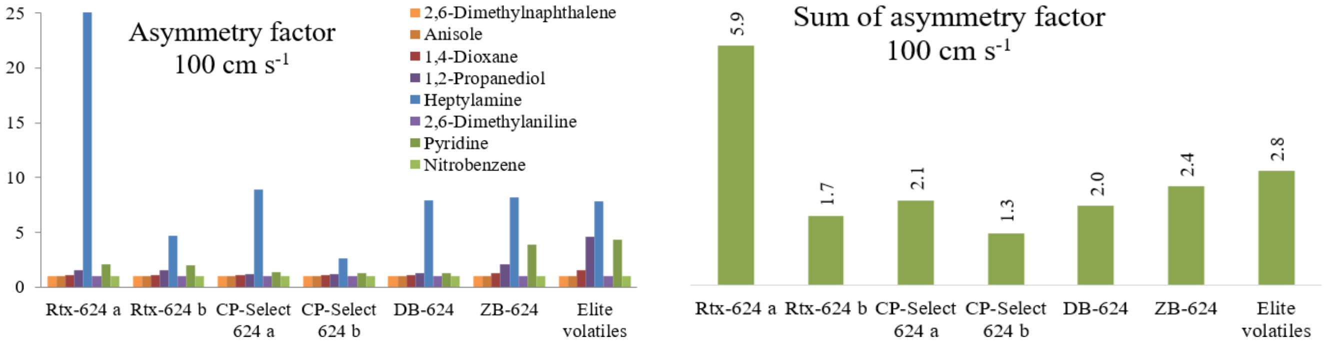
Fig. 2 Peak shape of pyridine on CP Select-624 b and Elite volatiles columns at 100 cm s^{-1}

differences are evidenced in comparison with the nearly symmetric ($A_s \approx 1$) peaks for pyridine, 1,2-propanediol, and heptylamine. Although the heptylamine peak has a tailing on every column there are significant differences between the extents of the tailing (The asymmetry factor of heptylamine changes in the range of 2,6 -38,3 at 100 cm s^{-1}). The difference in asymmetry for the pyridine peak at 100 cm s^{-1} measured on the CP-Select 624b (1.3) and the Elite Volatiles (4.3) column is shown in Fig. 2. These asymmetric peaks let us conclude the stationary phases are slightly acidic, which causes stronger reversible interactions with the amino and hydroxyl function groups. To show the effect of the stationary phase on the peak shape, we also represented the test solutes' average asymmetry factor for each column in Fig. 3 (b). Active points causing tailing resulted from the different manufacturing techniques and the history of the columns.

3.3 Effective carbon number

Since our previous studies show that *ECN* values depend on chromatographic parameters, the aim of our present study was not to reach the theoretical *ECN* values listed in Table 1. They served as a starting point for the approximate expected *ECN* values. In the present paper, we used the experimentally determined *ECN* values to illustrate the effect of the stationary phase on the quantification of different types of compounds.

The *ECN* values determined are shown in Table 3. For each compound, we marked the lowest *ECN* (ECN_{min}) and the highest *ECN* (ECN_{max}) values in italics and in bold,



(a) (b)

Fig. 3 (a) Asymmetry factor of the test compounds at 100 cm s^{-1} (Asymmetry factor of Heptylamin on Rtx-624 a column is 38.3); (b) Sum of asymmetry factors of the investigated columns at 100 cm s^{-1}

Table 3 The *ECN* values at 100 cm s^{-1}

	Rtx-624 a	Rtx-624 b	CP-Select 624 a	CP-Select 624 b	DB-624	ZB-624	Elite volatiles	Δ (max−min)	Δ(max−min) %
1,4-Dioxane	2.20	**2.23**	2.19	2.19	2.19	2.19	*2.15*	0.1	4%
Pyridine	4.81	4.67	4.75	**4.81**	4.64	*4.46*	4.66	0.4	7%
1,2-Propanediol	1.75	*1.32*	2.03	**2.04**	1.91	1.96	1.95	0.7	35%
Anisole	6.28	6.34	6.26	6.32	*6.23*	6.26	**6.38**	0.1	2%
Heptylamine	**6.12**	3.40	4.72	5.94	4.92	*2.54*	4.39	3.6	59%
Nitrobenzene	5.70	5.76	5.67	5.74	*5.45*	5.66	**5.81**	0.4	6%
2,6-Dimethylaniline	7.62	7.71	7.61	7.70	*7.50*	*7.58*	**7.86**	0.4	5%
2,6-Dimethylnaphtalene	11.14	**11.49**	11.24	11.31	*11.12*	11.16	11.20	0.4	3%
$\Delta ECN_{\text{column}}$	7.75	7.14	7.64	7.89	7.52	7.18	7.58		
Sequence Sum $\Delta ECN_{\text{column}}$	2	7	3	1	5	6	4		

The lowest *ECN* (ECN_{min}) and the highest *ECN* (ECN_{max}) values are marked in italics and in bold, respectively.

respectively. The difference between these two values displays the effect of the stationary phase on measuring the test compounds. The reduced *ECN* value is due to the irreversible interactions with the stationary phase, and the high Δ(max-min)% means significant differences in the stationary phase. These values let us differentiate the columns and help us choose the best column for the future target compounds. In our test molecules, the aromatic rings interact the same way with the stationary phases; however, with the non-hindered hydroxy and amino groups, some stationary phases form strong irreversible, instead of reversible, bonds. The highest Δ(max-min)% values were obtained for 1,2-propanediol and heptilamine.

Like in our previous work, we used the $\Delta ECN_{\text{column}}$ value to establish the order between the columns. The $\Delta ECN_{\text{column}}$ gives the average influence of the stationary phase on the *ECN*s.

$$\Delta ECN_{\text{column}} = \sum_i \frac{ECN_i}{ECN_{i,\max}} \tag{3}$$

In Eq. (3) ECN_i is the *ECN* value of the *i*-th solute on the stationary phase and $ECN_{i,\max}$ is the highest *ECN* value of the *i*-th compound on the 7 investigated columns. The theoretically achievable maximum score is 8 in the case of the 8 compounds. The established order of the columns is shown in Table 3.

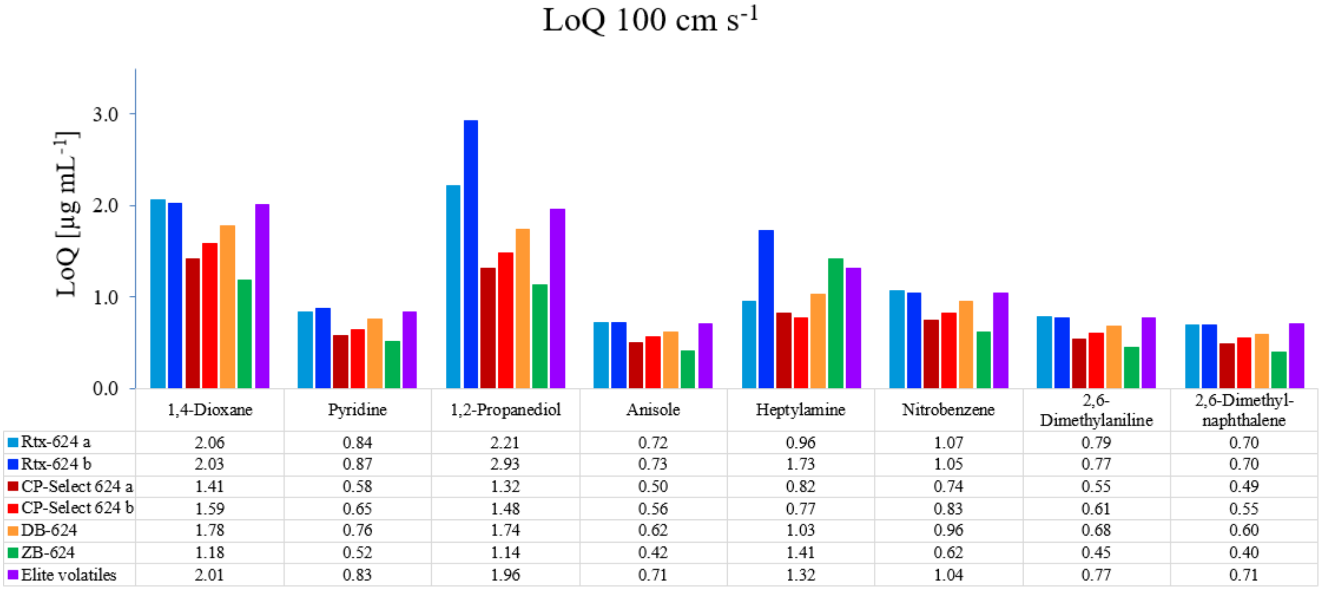
These results enable us to choose the best column in our laboratory for the measurements specific to diols, amines, heterocycles, or aromatic compounds.

3.4 Limit of quantitation

We determined the noise level on each column at each linear velocity to calculate the limit of quantitation with Eq. (4):

$$LoQ_i = 9 \times N_i, \tag{4}$$

where N_i is the mean area of the noise in mVs for the *i*-th solute. On every chromatogram, three different baseline sections were integrated. One-point calibration was used to convert the LoQ_i values into concentrations. Fig. 4. shows the limit of quantitation at 100 cm s^{-1} for the test components in µg mL^{-1} units. These differences can be attributed to two factors. As we concluded in our previous article, on the one hand, variance mainly derives from the different



	1,4-Dioxane	Pyridine	1,2-Propanediol	Anisole	Heptylamine	Nitrobenzene	2,6-Dimethylaniline	2,6-Dimethyl-naphthalene
🟦 Rtx-624 a	2.06	0.84	2.21	0.72	0.96	1.07	0.79	0.70
🟦 Rtx-624 b	2.03	0.87	2.93	0.73	1.73	1.05	0.77	0.70
🟥 CP-Select 624 a	1.41	0.58	1.32	0.50	0.82	0.74	0.55	0.49
🟥 CP-Select 624 b	1.59	0.65	1.48	0.56	0.77	0.83	0.61	0.55
🟧 DB-624	1.78	0.76	1.74	0.62	1.03	0.96	0.68	0.60
🟩 ZB-624	1.18	0.52	1.14	0.42	1.41	0.62	0.45	0.40
🟪 Elite volatiles	2.01	0.83	1.96	0.71	1.32	1.04	0.77	0.71

Fig. 4 Limit of quantitations of the test compounds for all investigated columns

detector responses manifesting in the *ECN* values of the components and is caused by irreversible interactions.

On the other hand, column bleeding increases the number of substances reaching the detector, consequently resulting in higher noise levels. This effect is related to the manufacturer's technology. In addition, at higher linear velocities an increased noise level was observed due to more molecules from the carrier gas entering the flame. The increased background noise levels also result in higher LoQ_i values.

4 Conclusion

The recent study is the continuation of our previous paper and concludes our investigation of the stationary phase equivalency research of seven 624-type gas chromatographic columns. In the previous study, ten different molecules were tested, while in the present paper, eight more were used to cover the gaps with more aromatic, heterocyclic, and nitrogen-containing compounds as well as basic molecules and a diol. By adding these molecules to the test mix, we can select more specifically the optimal column for our measurements.

We found remarkable differences in the retention order, peak shape, and peak area.

The retention order correlated with the manufacturers and enabled us to differentiate between "equivalent columns".

According to our results, the condition of the column stationary phase affects quantitative determination too. The reduction of the measurable peak area results from irreversible sorption, which we quantified by the decrease of the *ECN* value and increase of the *LoQ* value. The differences in area can be imputed both to different manufacturing technologies and the history of the columns. Impurities left over from previous measurements modify the surface of the stationary phase. Also, storage conditions can modify the stationary phase by humidity. The *LoQ* also contains information about column bleeding, which is also subject to manufacturing technology.

The *ECN* was an indicator of the irreversible sorption of non-hindered amines and diols on the stationary phase. Consequently, *ECN* loss is also a help in the proper column selection specific to the target compound characteristics.

Based on our results, even columns from the same manufacturer may not always be interchangeable.

In light of the presented results, a homemade test mixture and a couple of measurements in similar conditions can help the analyst select the optimal columns for the analytical task at hand. By means of tests repeated from time to time, the decomposition of the stationary phase can be monitored, ruling out measurements effected on a damaged, unsuitable column.

Acknowledgement
The authors thank B&B Analytics Ltd. (Érd, Hungary) for providing financial and technical support.

References

[1] Nyerges, G., Mátyási, J., Balla, J. "Comparison of 624-type Capillary Columns: "Equivalent Columns" Deviation in the Quantitative Analysis", Periodica Polytechnica Chemical Engineering, 67(3), pp. 427–434, 2023. https://doi.org/10.3311/PPch.21611

[2] Kováts, E. "Gas-chromatographische Charakterisierung Organischer Verbindungen. Teil 1: Retentionsindices Aliphatischer Halogenide, Alkohole, Aldehyde Und Ketone" (Gas chromatographic characterization of organic bonds Part 1: Retention indices of aliphatic halides, alcohols, aldehydes and ketones), Helvetica Chimica Acta, 41(7), pp. 1915–1932, 1958. (in German) https://doi.org/10.1002/hlca.19580410703

[3] Rohrschneider, L. "Eine Methode Zur Charakterisierung von Gaschromatographischen Trennflüssigkeiten" (One method for characterization of gas chromatographic liquid phases), Journal of Chromatography A, 22, pp. 6–22, 1966. (in German) https://doi.org/10.1016/s0021-9673(01)97064-5

[4] McReynolds, W. O. "Characterization of Some Liquid Phases", Journal of Chromatographic Science, 8(12), pp. 685–691, 1970. https://doi.org/10.1093/chromsci/8.12.685

[5] Wold, S. "Analysis of Similarities and Dissimilarities between Chromatographic Liquid Phases by Means of Pattern Cognition", Journal of Chromatographic Science, 13(11), pp. 525–532, 1975. https://doi.org/10.1093/chromsci/13.11.525

[6] Poole, S. K., Kersten, B. R., Poole, C. F. "Comparison of Solvent Models for Characterizing Stationary Phase Selectivity in Gas Chromatography", Journal of Chromatography A, 471, pp. 91–103, 1989. https://doi.org/10.1016/S0021-9673(00)94158-X

[7] Abraham, M. H., Whiting, G. S., Doherty, R. M., Shuely, W. J. "Hydrogen Bonding : XV. A New Characterisation of the McReynolds 77-Stationary Phase Set", Journal of Chromatography A, 518, pp. 329–348, 1990. https://doi.org/10.1016/S0021-9673(01)93194-2

[8] Abraham, M. H., Ballantine, D. S., Callihan, B. K. "Revised Linear Solvation Energy Relationship Coefficients for the 77-Phase McReynolds Data Set Based on an Updated Set of Solute Descriptors", Journal of Chromatography A, 878(1), pp. 115–124, 2000. https://doi.org/10.1016/S0021-9673(00)00143-6

[9] Grob J., K., Grob, G., Grob, K. "Comprehensive, Standardized Quality Test for Glass Capillary Columns", Journal of Chromatography A, 156(1), pp. 1–20, 1978. https://doi.org/10.1016/S0021-9673(00)83120-9

[10] Grob, K., Grob, G., Grob Jr., K. "Testing Capillary Gas Chromatographic Columns", Journal of Chromatography A, 219(1), pp. 13–20, 1981. https://doi.org/10.1016/S0021-9673(00)80568-3

[11] Horká, M., Kahle, V., Krejči, M. "Immobilized polyethyleneglycol-based stationary phase for the analysis of amines and organic acids by capillary gas chromatography", Journal of Chromatography A, 637(1), pp. 96–99, 1993. https://doi.org/https://doi.org/10.1016/0021-9673(93)83103-Y

[12] Dresen, R. J. M. N., Henderickx, H. J. W., Van Der Wal, S. "Capillary GC Column Performance Test for Basic Analytes", Journal of Microcolumn Separations, 10(8), pp. 661–669, 1998. https://doi.org/10.1002/(SICI)1520-667X(1998)10:8<661::AID-MCS5>3.0.CO;2-E

[13] Mehran, M., Cooper, W. J., Golkar, N., Nickelsen, M. G., Mittlefehldt, E. R., Guthrie, E., Jennings, W. "Elution Order in Gas Chromatography", Journal of High Resolution Chromatography, 14(11), pp. 745–750, 1991. https://doi.org/10.1002/JHRC.1240141109

[14] Nyerges, G., Mátyási, J., Balla, J. "Investigation and Comparison of 5 % Diphenyl – 95 % Dimethyl Polysiloxane Capillary Columns", Periodica Polytechnica Chemical Engineering, 64(4), pp. 430–436, 2020. https://doi.org/10.3311/PPch.15289

[15] Nyerges, G., Mátyási, J., Balla, J. "Analysis and Comparison of Gas Chromatographic Columns with Polyethylene Glycol Stationary Phase", Periodica Polytechnica Chemical Engineering, 67(2), pp. 185–192, 2023. https://doi.org/10.3311/PPch.21481

[16] Poole, C. F. "Gas Chromatography System Constant Database for 52 Wall-Coated, Open-Tubular Columns Covering the Temperature Range 60–140 °C", Journal of Chromatography A, 1604, 460482, 2019. https://doi.org/10.1016/j.chroma.2019.460482

[17] Becerra, M. R., Fernández-Sánchez, E., Fernández-Torres, A., Garciá-Domínguez, J. A., Santiuste, J. M. "Evaluation of the effect of the cyanopropyl radical on the interaction of the methylene group with silicone stationary phases", Journal of Chromatography A, 547, pp. 269–282, 1991. https://doi.org/10.1016/S0021-9673(01)88650-7

[18] Fernández-Sánchez, E., Fernández-Torres, A., García-Domínguez, J. A., Santiuste, J. M. "Kováts' Coefficients for Predicting Polarities in Silicone Stationary Phases and Their Mixtures", Chromatographia, 31(1), pp. 75–79, 1991. https://doi.org/10.1007/BF02290501

[19] Kiridena, W., Patchett, C. C., Koziol, W. W., Poole, C. F. "Assessment of the Selectivity Equivalence of DB-608 and DB-624 Open-Tubular Columns for Gas Chromatography", Journal of Separation Science, 27(15–16), pp. 1333–1338, 2004. https://doi.org/10.1002/jssc.200401862

[20] Caulfield, J. A., Bruno, T. J., Miller, K. E. "Enthalpy of Solution and Kováts Retention Indices for Nitroaromatic Compounds on Stationary Phases Using Gas Chromatography", Journal of Chemical & Engineering Data, 54(6), pp. 1814–1822, 2009. https://doi.org/10.1021/JE800851J

[21] Schofield, K. "The Enigmatic Mechanism of the Flame Ionization Detector: Its Overlooked Implications for Fossil Fuel Combustion Modeling", Progress in Energy and Combustion Science, 34(3), pp. 330–350, 2008. https://doi.org/10.1016/J.PECS.2007.08.001

[22] Sternberg, J. C., Gallaway, W. S., Jones, D. T. L. "The mechanism of response of flame ionization detectors", In: Gas Chromatography: Proceedings of the 3rd International Symposium Held Under the Auspices of the Analysis Instrumentation Division of the Instrument Society of America, Edinburgh, Scotland, 1962, pp. 231–267.

[23] Jorgensen, A. D., Picel, K. C., Stamoudis, V. C. "Prediction of Gas Chromatography Flame Ionization Detector Response Factors from Molecular Structures", Analytical Chemistry, 62(7), pp. 683–689, 1990.
https://doi.org/10.1021/ac00206a007

[24] Kállai, M., Veres, Z., Balla, J. "Response of Flame Ionization Detectors to Different Homologous Series", Chromatographia, 54(7), pp. 511–517, 2001.
https://doi.org/10.1007/BF02491209

[25] Kállai, M., Balla, J. "The Effect of Molecular Structure upon the Response of the Flame Ionization Detector", Chromatographia, 56, pp. 357–360, 2002.
https://doi.org/10.1007/BF02491945

[26] Perkins, Jr., G., Rouayheb, G. M., Lively, L. D., Hamilton, W. C. "Response of the Gas Chromatographic Flame Ionization Detector to Different Functional Groups", In: Gas Chromatography: Proceedings of the 3rd International Symposium Held Under the Auspices of the Analysis Instrumentation Division of the Instrument Society of America, Edinburgh, Scotland, 1962, pp. 269–285.

[27] Kállai, M., Máté, V., Balla, J. "Effects of Experimental Conditions on the Determination of the Effective Carbon Number", Chromatographia, 57(9), pp. 639–644, 2003.
https://doi.org/10.1007/BF02491742

[28] Mátyási, J., Zverger, D., Gaál, B., Balla, J. "The Effect of the Linear Velocity on the Detector Response and Effective Carbon Number: The Role of the Experimental Conditions in the Quantitative Analysis", Periodica Polytechnica Chemical Engineering, 65(2), pp. 158–166, 2021.
https://doi.org/10.3311/PPch.16130

[29] Scanlon, J. T., Willis, D. E. "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept", Journal of Chromatographic Science, 23(8), pp. 333–340, 1985.
https://doi.org/10.1093/chromsci/23.8.333