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Comparison of 624-type Capillary Columns

"Equivalent Columns" Deviation in the Quantitative Analysis

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Abstract

In our research, seven 624-type capillary columns were investigated. All the columns were the same in length, internal diameter, and film thickness (30 m × 0.32 mm × 1.0 µm). However, they were produced by different manufacturers or the same manufacturer but in different batches. Even though the manufacturers recommend them as "equivalent columns" this equivalence did not prevail even in the case of columns produced by the same manufacturer. Our examination criteria centered on the quantitative determination ability of the columns. A homemade column test mixture was compiled to represent all the second-order interactions that can occur between the analyte and stationary phase. Although theoretically these columns have the same stationary phase quality, they did not result in the same chromatograms. In addition to the origin and batch of the column, the "history of the column" contributes likewise to the different peak symmetry, retention order, and even peak areas that affect the quantitative determination. We quantified this quantitative determination ability with the effective carbon number (ECN) and the Limit of Quantitation (LoQ) values. Based on our results the attainable LoQ and ECN values depend at least as much on the origin and actual state of the stationary phase as on the measurement conditions to be optimized. In our paper, we demonstrate the extent to which the same stationary phases offered by different companies and/or different backgrounds can influence our detection limit and detector response even if the relevant columns have theoretically the same chemical structure.

Keywords

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

1 Introduction

With a large proportion of gas chromatography procedures, the key element is the implementation of the best limit of quantitation (LoQ). Generally, to reach the lowest LoQ value, gas chromatographers put their best effort into trying to optimize the measurement parameters (injector and detector temperature, linear velocity, column oven temperature program, mode of injection, detector type, quality of stationary phase, etc.). However, the best available LoQ is subject to the prior selection of columns. With our study, we want to demonstrate that the specific column on which the development is carried out sets the limit in development because the theoretically right-chosen stationary phase does not guarantee the perfect chromatographic determination itself in practice.

The selection of the proper gas chromatographic column has a crucial role in the success of qualitative and quantitative analysis. The consideration of column parameters that affect efficiency (column length, internal diameter, film thickness) is preceded by a decision on the appropriate type of stationary phase, which, in addition to the selectivity of the separation, ensures that there are second-order interactions appropriate to the target compounds.

In our decision we can rely, on the one hand, on information provided by the column manufacturer. Databases of different column producers provide us with a huge amount of application notes and technical reports. These sources even give information regarding column equivalency, i.e., which column can replace another manufacturer's column with the same effectiveness. Even though column production is a complicated multi-step procedure that includes treating and deactivation of the silica surface, wall-coating, and immobilization of the stationary

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phase. These steps are implemented by the manufacturers using different technologies giving rise to different qualities of the stationary phase [1, 2].

On the other hand, we can check the literature for the characterization of stationary phases by different methods. However, the starting point for all these methods is based on the retention data of some compounds chosen as a representative of the individual second-order interaction which can occur between the analyte and stationary phase under a gas chromatographic separation. In his article published in 1966, Rohrschneider characterized the polarity of 22 stationary phases with differences in the retention index of 5 model components, which were benzene, ethanol, ethyl methyl ketone, nitromethane, and pyridine [3]. The reference value against which the difference was measured was provided by the indices of the model compounds measured on the apolar squalane stationary phase. With these test compounds, he covered the second-order interactions, like dispersion, Π-Π, and induction interaction, electron pair acceptor and electron-pair donor behavior. This method was further developed in 1970 by McReynolds [4], who partly replaced the test compounds and partly expanded them. The McReynolds constants (MRc) are widely used for describing the polarity of gas chromatographic stationary phases, providing an opportunity for uniformized comparison. A scale was defined from 0 to 100 for the chromatographic polarity index (CPI), where the squalane represents the most apolar zero point and the 100% cyanopropyl siloxane phase represents the most polar 100 value. The certain stationary phase according to the MRc values measured can be placed on the scale between 0 and 100. Many authors categorized the huge amount of chromatographic data collected by McReynolds based on different considerations (retention indices for 376 compounds measured on 77 stationary phases at two temperature levels, retention indices for 10 compounds on 226 stationary phases) [5]. In 1990 Abraham et al. introduced the solvation parameter model to describe McReynolds 77-stationary phase set with 5 constants instead of one single polarity index [5]. Based on the solvation parameter model Poole [1] built up a chromatography system constant database for 52 wall-coated capillary columns using multiple linear regression analysis.

For the long-established stationary phases, we can use these column polarity sets as a starting point. However, daily chromatographic routine confronts us with the differences between theory and practice. Even if we use a general phase, as a consequence of different manufacturing techniques differences will appear in the chromatographic separation, to say nothing about application-specific stationary phases whose composition is covered by industrial secrecy.

For user column testing specifically the Grob test mixes introduced by the Grob family [6, 7] are in widespread use. These mixtures went through changes in composition through the years. When used with test compounds they displayed separation efficiency, excess sorption in the injector, loss of stationary phase through bleeding, sorption of the hydroxyl group and the aldehyde group, and the acid-base effect. They can be used for apolar and polar phases too, requiring only one single injection. A typical composition contains the following compounds: methyl decanoate, methyl undecanoate, methyl dodecanoate, *n*-decane, *n*-undecane, *n*-dodecane, 1-octanol, nonanal, 2,3-butanediol, 2,6-dimethylaniline, 2,6-dimethylphenol, dicyclohexylamine, 2-ethylhexanoic acid where methyl esters and alkanes are used as a reference [6, 7].

Nevertheless, in specific cases like the separation of basic analytes, the modification of the mix is necessary because of the irreversible sorption of the reference compounds on the basic-modified stationary phases [8]. To this day, many column manufacturers attach chromatograms of these Grob-mixtures to the particular column they are selling as a certificate. In other cases, manufacturers use their own test mixtures. Although the manufacturer's test mixture developed for the given stationary phase is more specific than the universal Grob-mixture, one advantage of using them is that the user's outcome is comparable with the test chromatogram included in the column box [9].

In our previous study, we compared equivalent 5% diphenyl – 95% dimethyl polysiloxane capillary columns reaching the conclusion that they show differences in enthalpy, entropy, retention, peak shape, and efficiency for the investigated compounds [10]. In addition, in our present study, we want to show how the column manufacturer and prelife affect the detector response signal, i.e., the effective carbon number, and thus the extent to which the lower limit of quantitation is influenced.

"624" columns (6% cyanopropylphenyl-94% dimethylpolysiloxane) are recommended for the separation of volatile organic pollutants and residual solvents, due to the different dipole-type interactions in addition to dispersion interaction. The Elite-Volatiles column is recommended for the analysis of volatile organic pollutants. Even though the composition of the stationary phase is withheld from the users it is offered as an equivalent column with the 624-type columns [11].

Due to the cyano group, the 624 stationary phases can take part in dipole-dipole, dipole-induced dipole interactions and can form a hydrogen bond as a hydrogen acceptor. Due to phenyl groups, Π-Π and induction interaction can be formed.

For our experiments, we prepared a test mixture containing compounds that represent all of the molecular interactions that are possible in the gas chromatographic separation system. At the same time, we applied compounds that represent basic and acidic interactions as well. Although the examined stationary phase, in theory, is not able to form acidic interaction where a hydrogen bond participates as an electron pair acceptor, we assumed all of the interactions to be in line with our earlier experience [12].

Kiridena et al. [13] described this stationary phase with the help of the solvation parameter model.

To characterize our columns, in addition to the peak asymmetry we used the elution order of the solutes too. However, retention order is not included among the criteria of column equivalency because it depends on the program rate and applied linear velocity [14]. We used the same chromatographic parameters to avoid this contradiction in every case.

The response of the flame ionization detector (FID) detector is proportional to the specific carbon number of the compound in the case of hydrocarbons [15]. The signal-producing behavior is based on the excited state of CH* radicals forming in the diffusion hydrogen flame [16]. The FID is also called a "carbon-counting" detector [17]. In the case of heteroatom-containing compounds the detector signal magnitude differs from the signal magnitude usual for hydrocarbons.

To characterize the detector response of the different species, Sternberg introduced the effective carbon number concept by Eq. (1):

$$\mathrm{ECN}_i = n_s \frac{A_i}{A_s}\frac{m_s}{m_i}\frac{M_i}{M_s} = n_s f_i \frac{M_i}{M_s}, \quad (1)$$

where n is the carbon number, A is the peak area, m is the weight of the substance, M is the molar mass, i is the investigated compound, s is the standard compound and f is the relative response, respectively.

The characteristic signal-reducing constants of the heteroatoms in different chemical bonds are available in the literature [15, 18–20].

The dependence of the effective carbon number on different chromatographic experimental conditions like column, injector and detector temperature, mode of the injection, linear velocity, and the circumstances of sample preparation like analyte concentration and quality of the reference compound was investigated in our previous studies [21, 22]. And even if the ECN value is subject to chromatographic parameters, with its help we can test the stationary phases [23]. Reduced ECN value refers to irreversible excess sorption on the stationary phase.

Based on our experience in extreme cases the whole peak could be missing from the chromatogram due to the strong first-order chemical interactions. Missing peak is a highly indicative tool of stationary phase state. Column activity originating from production and contamination have the same effect: missing peak.

The quantitative determination ability of the columns was characterized by ECN and LoQ values.

2 Experimental

2.1 Reagents

We selected 10 different test compounds displayed in Table 1. Normal alkanes (C_7, C_8, C_9, C_{11}, C_{13}, C_{22}) were used as references for ECN calculations.

All of the investigated compounds are able to form dispersion interaction and can take a part in dipole-dipole interaction except Ethylbenzene. We used aromatic compounds: ethylbenzene, 2,6-dimethylphenol and o-toluenesulfonamide for the representation of Π-Π interaction. Molecules that have acidic character were valeric acid, 1-pentanol and 2,6-dimethylphenol. Caffeine and *o*-toluenesulfonamide were used as basic compounds. All components can behave as electron pair donors. 1-Pentanol, 2,6-dimethylphenol, valeric acid and *o*-toluenesulfonamide are able to behave as electron pair acceptors too.

The standards were purchased from Sigma-Aldrich. Approximately 25 mg of the substances were added into a 25 mL volumetric flask and diluted with acetone. 1 mL from the stock solution was added into a 20 mL measuring flask and was diluted with acetone. The final concentration was around 50 μg mL^{-1} for each analyte.

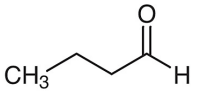
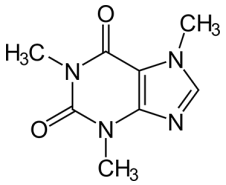
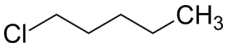
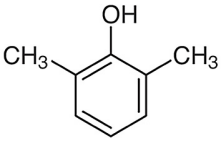
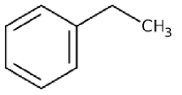
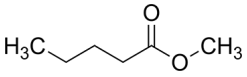
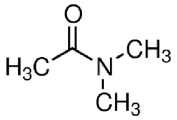
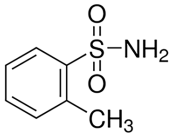
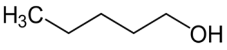
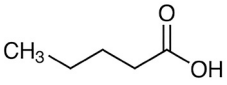
2.2 Columns

The 7 investigated columns are shown in Table 2. The column length, the internal diameter and the film thickness was 30 m, 0.32 mm and 1.0 μm, respectively for every column. The columns were used for various analytical problems before. Prior to testing the columns were conditioned.

2.3 Apparatus

A Shimadzu GC-2014 gas chromatograph equipped with a Shimadzu AOC-20i autosampler was used. A single ramp (5 °C min^{-1}) oven temperature program from 40 °C with no

Table 1 Test compounds

No.	Compound name	ECN theoretic	Structure
1	Butyraldehyde	3[1]	
2	Caffeine	3.92[2]	
3	1-Chloropentane	4.86	
4	2,6-Dimethylphenol	7.36[2]	
5	Ethylbenzene	6.88	
6	Methyl pentanoate	4.51	
7	*N*,*N*-Dimethylacetamide	2.75[1]	
8	*o*-Toluenesulfonamide	6.21	
9	1-Pentanol	4.56	
10	Valeric acid	4[3]	

[1] Sternberg et al. [15], [2] Jorgensen et al. [18], [3] Perkins et al. [20]

Table 2 Test 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

initial temperature plateau was applied. The final temperature was 250 °C and was held for 10 min. The GC injector and the detector temperature were 250 °C. 1 µL was injected from each vial five times. The split ratio was 20:1. Nitrogen (purity 99.996%) was used as the make-up gas, and the applied pressure was 75 kPa. Air and hydrogen pressure (purity 99.98%) applied to the flame ionization detector was 50 kPa and 60 kPa, respectively. Hydrogen was used as the carrier gas with linear velocity control. The measurements were carried out at four linear velocity levels (50, 100, 150, and 200 cm s^{-1}). The liner was silylated before use to eliminate excess sorption in the injection port.

2.4 Effective carbon number

We calculated the theoretical ECN numbers (Table 1) of the test compounds based on our previous study [19]. In case we had no experimentally determined effective carbon number increments on hand, we used increments available in the literature [15, 18, 20]. The ECN values were calculated from the actual carbon number by subtracting the ECN increments belonging to each functional group. In the case of $–SO_2–$ group no data was found in the literature.

3 Results and discussion

3.1 Retention order

Chromatograms of the investigated compounds are shown in Fig. 1 where the alkanes used as reference components also appear. Although the "retention distances" differed to a small extent, the retention order was the same for all investigated columns except the Elite-Volatile column. It is conspicuous in Fig. 1 that the retention times of the reference alkanes (peaks 2, 4, 8, 11, 13 and 16) measured on the Elite-Volatiles column are approximately the same as that measured on all other columns. However, all of the test compounds have the ability to take part in a dipole-type interaction even with more functional groups having a lesser extent of retention on this stationary phase. All of the test compounds "are being shifted forward" on the chromatogram, while the reference alkanes, which are only capable of creating a dispersion interaction, remained at the same "retention place". On the Elite-Volatiles column the following retention order change appeared: 1-pentanol (5) preceded *n*-octane (4), valeric acid preceded *n*-nonane (8), and *N*,*N*-dimethylacetamide (9) too. Valeric acid (10) is coeluted with ethylbenzene (7). With other linear velocity values applied, no coelution occurred on any column. Valeric acid (10) did not appear on the CP-Select 624 b column.

3.2 Peak symmetry

The peak shape of the test compounds was described with the asymmetry factor. Calculations were carried out with Eq. (2):

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

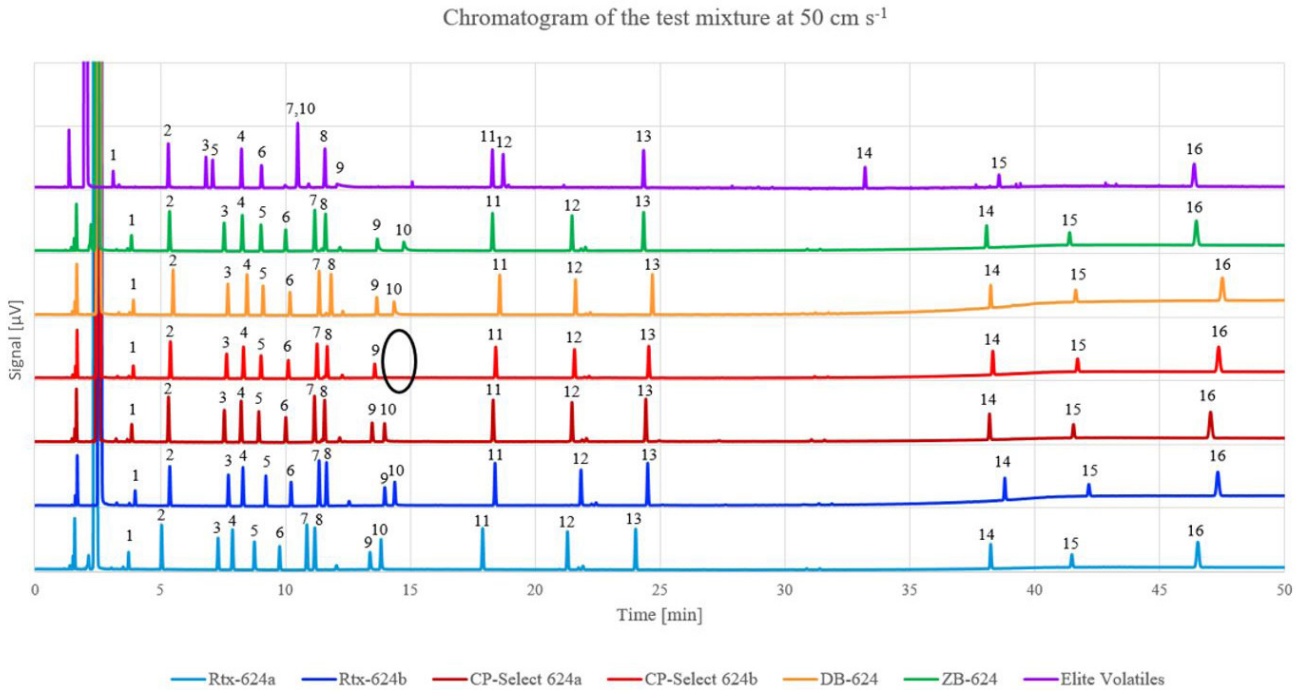


Fig. 1 Chromatogram of the test mixture on the investigated columns: 1 – Butyraldehyde, 2 – *n*-Heptane, 3 – 1-Chloropentane, 4 – *n*-Octane, 5 – 1-Pentanol, 6 – Methyl Pentanoate, 7 – Ethylbenzene, 8 – *n*-Nonane, 9 – *N*,*N*-Dimethylacetamide, 10 – Valeric Acid, 11 – *n*-Undecan, 12 – 2,6-Dimethylphenol, 13 – *n*-Tridecane, 14 – *o*-Toluenesulfonamide, 15 – Caffeine, 16 – *n*-Docosane

where A_s is the asymmetry factor, *b*, is the distance from the peak midpoint to the end of the peak and *a* is the distance from the start of the peak to the peak midpoint, where *a* and *b* are measured at 10% peak height. The midpoint is defined by the highest point of the peak. Almost without exception, we obtained asymmetry factors greater than 1 for test compounds, i.e., tailing peaks. For significant symmetry difference, there is an example in Fig. 2 where the asymmetry factor of *N*,*N*-dimethylacetamide is 1.3 for CP-Select 624 and 10.9 for Elite-Volatiles column under the same chromatographic conditions. For describing the effect of the stationary phase on the peak shape we displayed the sum of the asymmetry factors of each test compound for the given column in Fig. 3. In the asymmetry factor, the reversible excess sorption appears to be caused by active points of the stationary phase originating from column manufacturing techniques or from the contaminations from the prelife of the column. With the increasing asymmetry factors, the inertness of the stationary phase surface will decrease.

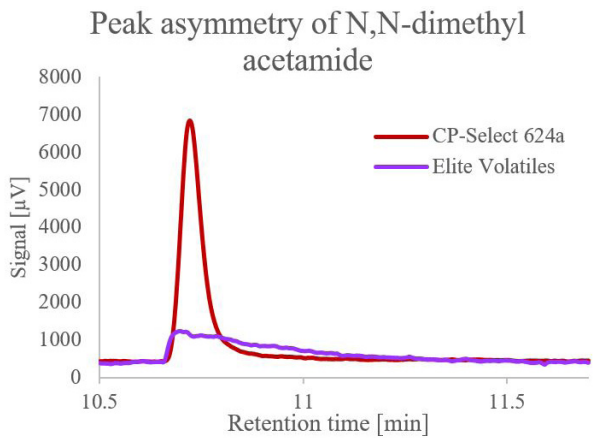


Fig. 2 Peak shape of of *N*,*N*-dimethylacetamide on CP-Select 624a and Elite-Volatiles column at 100 cm s^{-1}

3.3 Effective carbon number

In Table 1 we indicated the theoretical ECN values of the investigated compounds. In our earlier investigations, we found that ECN significantly depends on chromatographic parameters. Therefore, we assumed, that our measured ECN values will deviate from the theoretical values.

We did not aim to reach the values shown in Table 1. We used the ECN concept to demonstrate the conspicuous detector response differences caused by the state of the stationary phase. In Table 3 calculated ECN values are displayed. The highest calculated ECN value (ECN_{MAX}) is marked in bold, and the lowest ECN value (ECN_{MIN}) is marked in italics for each compound. We defined a coefficient ΔECN_{column} (Eq. (3)) for describing the whole impact of the column stationary phase on ECN.

$$\Delta ECN_{column} = \sum_i \frac{ECN_i}{ECN_{i,MAX}}, \quad (3)$$

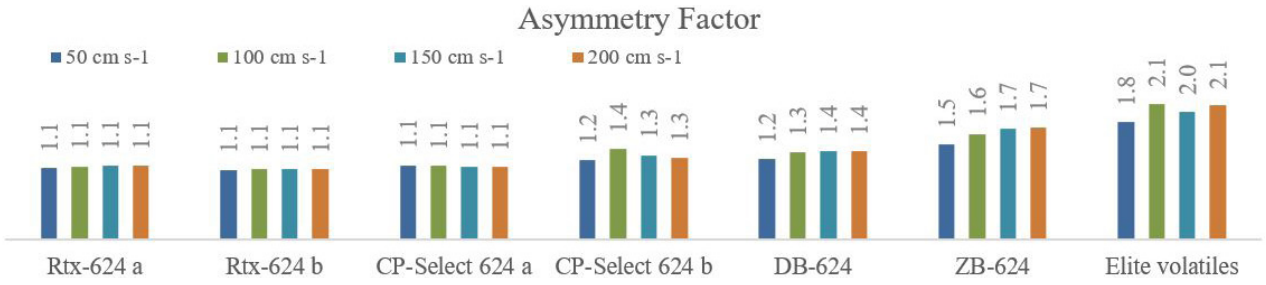


Fig. 3 Sum of asymmetry factors of the investigated columns at different linear velocity values (50, 100, 150, and 200 cm s^{-1})

Table 3 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) %
Butyraldehyde	3.71	3.52	3.58	3.40	*3.17*	3.63	**3.82**	0.7	17%
1-Chloropentane	**5.21**	5.16	5.16	*5.14*	5.17	5.17	5.17	0.1	1%
1-Pentanol	4.75	4.75	**4.79**	4.78	*4.72*	*4.72*	4.76	0.1	1%
Methyl pentanoate	4.84	4.83	**4.86**	4.78	4.78	4.81	*4.74*	0.1	2%
Ethylbenzene	8.50	8.37	8.40	8.39	*8.34*	8.37	**8.54**	0.2	2%
N,*N*-Dimethylacetamide	2.53	2.47	2.55	**2.56**	2.53	2.53	*2.38*	0.2	7%
Valeric acid	**3.90**	3.46	2.95	*0.59*	3.02	2.80	3.65	3.3	85%
2,6-Dimethylphenol	7.54	*7.29*	7.77	**7.96**	7.68	7.55	7.91	0.7	8%
o-Toluenesulfonamide	6.17	6.02	**6.42**	6.03	6.19	*5.98*	6.29	0.4	7%
Caffeine	*4.33*	4.36	**4.59**	4.40	4.43	4.46	4.49	0.3	6%
ΔECN_{column}	9.8	9.5	9.6	8.9	9.4	9.5	9.8		
Sequence Sum ΔECN_{column}	1	4	3	7	6	5	2		

where ECN_i is the measured ECN value of the test compound on the investigated column, $ECN_{i,MAX}$ is the highest ECN value for the test compounds measured on the 7 columns. The theoretical maximum score of coefficient ΔECN_{column} in the case of 10 test compounds is 10. The sequence of the columns is shown in the last line in Table 3. Fig. 4 displays the dependency of the ECN value on the linear velocity. ECN of *o*-toluenesulfonamide takes a different value at different velocity values. However, the tendency of the alteration depends on the column applied. In the case of Rtx-624 a, Rtx-624 b and Elite-Volatiles columns the ECN decreases with the increase in velocity. By contrast, in the case of CP-Select 624 a, CP-Select 624 b, DB-624 and ZB-624 columns, the ECN increases with the increase in velocity. It is notable that columns produced by the same manufacturer have the same behavior. Decreased ECN values indicate irreversible excess sorption on the stationary phase. The highest Δ (MAX-MIN) % values were obtained for butyraldehyde, *N*,*N*-dimethylacetamide, valeric acid, 2,6-dimethylphenol, *o*-toluenesulfonamide and caffeine. These results are the consequence of the acidic and basic stationary phase surface.

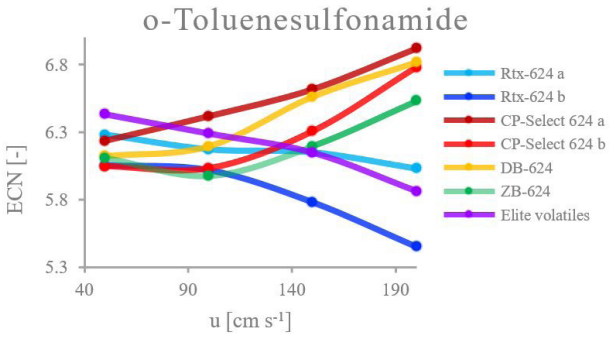


Fig. 4 Dependency of ECN of *o*-toluenesulfonamide on the linear velocity

Based on these results we can select the best of our column stock for our future analyses suited for aldehydes, amides, acids, sulfonates, or nitrogen containing heterocycles.

3.4 Limit of quantitation

For the calculation of the limit of quantitation, we determined the noise level at each column at each linear velocity. Equation (4) was used:

$$LoQ_i = 9 \times N_i, \quad (4)$$

where N is the area of noise in mVs unit and i is the i-th compound. 3 noise peaks were integrated in every case from the sample runs at the middle section of the chromatogram. N values were converted to concentration with one-point calibration. Two effects influence LoQ. One is

the noise level that assumed a similar value at low linear velocity for all columns. Increasing the carrier gas linear velocity resulted in an increase in noise level and increased the differences between the columns. At higher linear velocity a higher amount of substance appears in the flame originating from the amount of the carrier gas molecules and the stationary phase bleeding. The other effect that influences the LoQ is the detector response, the ECN of the particular substance. This effect has an impact of greater extent on LoQ, which is seen in Fig. 5.

4 Conclusion

Our investigation aimed to test and compare the 624-type columns of our column stock. We have compiled a homemade test mixture to represent all of interactions that can appear between the analyte and stationary phase, thus testing which components of the given stationary phase are suitable for determination. We found a significant alteration in retention order, peak asymmetry, and peak areas between the investigated columns. We expressed the significant differences in peak areas quantified by the effective carbon number and the limit of quantitation values. LoQ, the basis of quantitative analysis, depends on the manufacturer's column-producing technique and column history. Because the different column manufacturers apply different techniques, this fact entails the consequence that the detection limit of the developed analytical quantification method will depend on which manufacturer the column is purchased from, even if the manufacturers label their products as "equivalent" to other manufacturer's products. LoQ level reflects on the extent of column bleeding, which is again a question of the manufacturer's production technique. The other crucial effect is the prelife of the column. The contaminations remaining on the stationary phase surface come from previous samples that modified the sorption behavior of the column, consequently, such columns act like other types of stationary phase.

We characterized the effect of the column stationary phase on the quantitative measurements with effective carbon number too. In our earlier studies, we have demonstrated how ECN depends on different gas chromatographic parameters. In this study, we described that ECN depends on the quality of the stationary phase, thus the manufacturer and column history. Decreased ECN values reflect the irreversible sorption of the stationary phase. Based on this ECN-loss, it is possible to make a decision as to which column to choose from our own column stock that is best suited for the investigated compound class (aldehydes, acids, amides, etc.).

In this paper, we demonstrated the altered behavior of 7 theoretically equivalent columns. Even if the columns are claimed to have column-to-column reproducibility by the manufacturer and to be interchangeable for validated methods, they are not interchangeable in every case.

Homemade test mixtures are useful and beneficial for monitoring the state of the stationary phase which is determined by the combined effect of the manufacturing technology and the impact of samples measured previously on the column.

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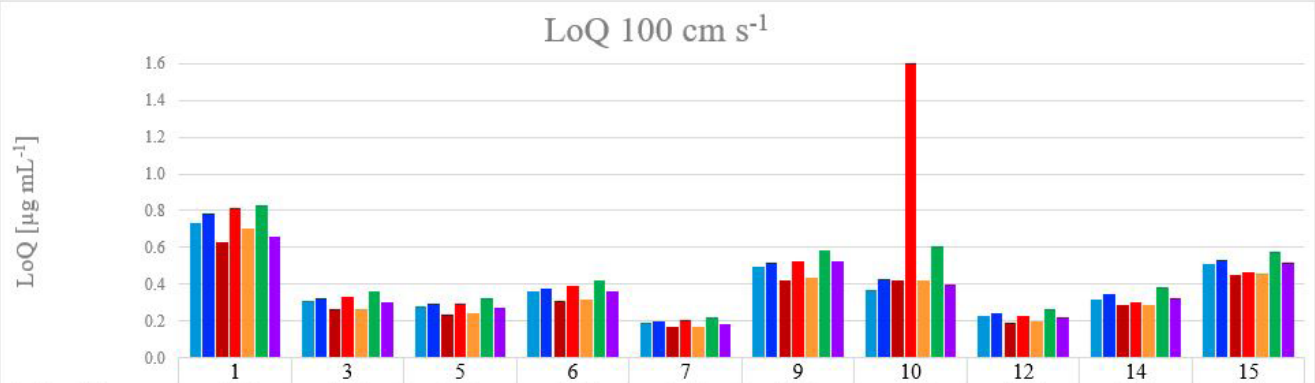

	1	3	5	6	7	9	10	12	14	15
Rtx-624 a	0.73	0.31	0.28	0.36	0.19	0.49	0.37	0.22	0.31	0.51
Rtx-624 b	0.78	0.32	0.29	0.37	0.20	0.52	0.43	0.24	0.34	0.53
CP-Select 624 a	0.62	0.26	0.24	0.31	0.16	0.42	0.42	0.19	0.28	0.45
CP-Select 624 b	0.81	0.33	0.29	0.39	0.20	0.52	2.64	0.22	0.30	0.46
DB-624	0.70	0.26	0.24	0.31	0.16	0.43	0.42	0.20	0.29	0.45
ZB-624	0.82	0.36	0.32	0.42	0.22	0.58	0.60	0.26	0.38	0.58
Elite volatiles	0.66	0.30	0.27	0.36	0.18	0.52	0.39	0.21	0.32	0.51

Fig. 5 Limit of quantitations of the test compounds for all investigated columns

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