

The Effect of the Linear Velocity on the Detector Response and Effective Carbon Number: The Role of the Experimental Conditions in the Quantitative Analysis

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Abstract

Since its introduction in 1957 the Flame Ionization Detector (FID) is the most widely used Gas Chromatographic (GC) detector. Nowadays there is no Gas Chromatographic laboratory without apparatus containing a Flame Ionization Detector. However, the operation mechanism of the hydrogen flame and signal production is still not completely obvious. The FID response for hydrocarbons is proportional to the carbon content of the compound, while substances that contain heteroatoms yield smaller responses. In the Gas Chromatographic practice, a special relative response factor called Effective Carbon Number (ECN) is used for the expression of the response for molecules containing heteroatom. In the literature there are signal modifying constants published by different authors, which are typical of the carbon atoms and heteroatoms in the different chemical bonds. Although these constants express the nature of the modification (increase or decrease) the exact modifying value always depends on the chromatographic parameters and the molecular structure. If we want to apply the ECN method for our calculations these constants should be determined for our specific Gas Chromatographic system. In our earlier study we investigated the effect of the temperature of the injector, column and detector, the mode of the injection and the concentration level of the substance. The aim of this paper is to investigate the effect of the linear velocity on the response of the Flame Ionization Detector as a mass flow rate sensitive detector in the case of capillary column.

Keywords

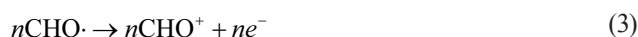
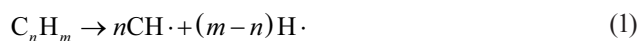
Effective Carbon Number (ECN), linear velocity, capillary column, Flame Ionization Detector (FID)

1 Introduction

The ultimate aim of the analytical separations is the qualitative and/or quantitative determination of the analyte. For this purpose, in the case of the Gas Chromatographic quantitative analysis pure authentic standards are used to determine the sensitivity of the analyte experimentally. The determination of the sensitivity is a routine procedure if a Gas Chromatographic standard commercially available. In case the standard is not available for detector calibration, that is a problem that should be solved in an alternative way. In the case of CLASS compounds (Compounds Lacking Authentic Standards or Surrogates [1]) the calculation of the sensitivity instead of the experimental determination could be a solution.

With calculations we can predict a response for the CLASS compounds but for predictions we need to know the signal production mechanism of the detector. From the

early 60's numerous investigations postulated principles about the radical chain reaction in the laminar diffusion flame, the formation of the charged carriers, the mechanism of detection and the detector response dependency on the molecular structure and the chromatographic parameters; however the chemical and physical processes by which it operates are still not known in detail and a predominant part of the experimental data originates from the observation of the FID without separation [2, 3] or from packed column conditions [4–8]. An important paper written by Sternberg et al. [2] in 1962 is a source of excessive number of accepted facts describing the procedure taking place in the hydrogen flame. According to this paper the combustion of the organic compounds undergoes with chemical ionization. The three main steps that produce electrical current are pyrolysis, oxidation and ionization (Eqs. (1)–(3)).



After the compounds leave the end of the column, they go through the preheating zone and step into the oxygen deficient area of the flame. Cracking occurs and radicals appear in the first step. A radical chain reaction starts. When they step into the oxygen rich area of the flame, oxidation happens. Electrical signal is provided by the production of the charged species. In the last step the electrical circuit closes between the two electrodes applied in the FID. The current is proportional to the carbon content of the compounds. In the case of hydrocarbons, the detector's molar response is proportional to the specific carbon number of the compound. For this reason, FID is also called a "carbon counting detector" and the signal evaluation is described with the "equal per carbon rule" expression [9]. Behind this expression was the assumption that from all molecules is formed exactly the same "one carbon fragment" in the flame. And this fragment is the unit of the signal production. In the literature the "one carbon fragment" theory appeared in different sources to support the observations with the responses of alkanes. In some cases, only the assumption of the existence of the one carbon quantum is published [2] but in other papers the assumption of the certain "universal one carbon fragment" is described as the methyl radical [9, 10] or methane [11, 12]. In 1999 Holm [13] showed their results about the investigation of the laminar hydrogen flame by mass spectrometer. Introducing compounds into the flame they measured the formed fragments in different parts of the flame during the whole combustion process. According to their results they found that hydrogenolysis happened in the flame and methane was formed. Methane formation was quantitative in the case of the investigated compounds with different molecular structures like benzene, ethyne or isobutane. Thus the earlier assumption seemed to be proved, the methane is the "universal one carbon fragment" and the "equal per carbon rule" was explained.

In 2008 Schofield [14] summarized the latest findings and achievement about the nature of the diffusion hydrogen flame of the FID detector. After many "speculative suggestion" the mechanism of signal production has been resolved. The carbon counting behaviour of the FID was described. The main step in chemi-ionization is the reaction of ground state CH fragment and atomic O.

Understanding the detector response of the non-hydrocarbons is more difficult. Molecules containing heteroatoms have less response in the flame than hydrocarbons with equal carbon content. From these types of compounds different small species leave the flame without ion and current production. Oxygen-, nitrogen- and halogen-containing compounds produce carbon monoxide, hydrocyanic acid and hydrogen halides in the flame, respectively [12]. The amount of these species depends on the molecular structure. The response modifying effect of the different heteroatoms in different types of bonds was investigated by several research groups [2, 15, 16]. Overall tables are published containing the characteristic signal reducing constants of the different compound groups. It is common practice to express the modifying effect with the use of Effective Carbon Number (ECN):

$$ECN_i = n_s \frac{A_i/N_i}{A_s/N_s}, \quad (4)$$

where A is the peak area, n is the carbon number, N is the amount of the substance, i is the investigated compound, s is the standard compound respectively. By substituting the well-known relation:

$$N = \frac{m}{M}, \quad (5)$$

where m is the weight and M is the molar mass, we achieve the following equation:

$$ECN_i = n_s \frac{A_i}{A_s} \frac{m_s}{m_i} \frac{M_i}{M_s} = n_s f_i \frac{M_i}{M_s}, \quad (6)$$

where f is the relative response.

The ECN value can be interpreted from another aspect as the sum of the ECN increments:

$$ECN_i = \sum_{j=1}^n ECN_j, \quad (7)$$

where ECN_j is the effective carbon atom number increments of the different atoms or atom groups present in the molecule. If there is only one heteroatom or functional group in the compound it is easy to express its increment.

$$ECN_j = \Delta ECN = ECN_i - n_{c,i}, \quad (8)$$

where $n_{c,i}$ is the actual carbon atom number of the molecule.

ΔECN values published by different research groups are shown in Table 1.

Mainly authors publish the different ΔECN values as universal constant for the specific compound class and

Table 1 Δ ECN values published by different authors

Class	Sternberg et al. [2]	Jorgensen et al. [15]	Kállai et al. [16]
	Average Δ ECN	Average Δ ECN	Average Δ ECN
Normal alkanes	0	-0.08	-0.02
Aromatic hydrocarbons	0	-0.08	-0.54/-1.12
Halogenated aromatic hydrocarbons	0	-	-0.55
Chloroalkanes	0	-	-0.14
Bromoalkanes	0	-	-0.25
Iodoalkanes	0	-	-0.14
Primary alcohols	-0.6	-0.64	-0.72
Amines	-0.6	-0.58	-0.79
Esters	-1.25	-1.27	-1.49
Ketones	-1.0	-0.80	-0.99

what we can use under any circumstances for our own measurement. However, our earlier study demonstrates [17] that these Δ ECN values show dependency on the different chromatographic parameters. We found that the injector, detector and column temperature, the injection mode, the concentration of the substance and the quality of the reference compound also have effect on the ECN values of different model substances. It confirms that it is required to build up our own ECN collection if we want to use it for quantitative analysis.

Due to the Flame Ionization Detector being a mass flow rate sensitive detector we would assume, that the signal of the investigated compound is independent from the linear velocity [18], so the area under the peak - produced by the substance - is the same at different velocity levels and depends only on the sum amount of the substance which reaches the flame independently from the elapsed time that takes the substance to go through the detector.

Authors published experimental data with different conclusions. Some of the research groups reported observations that the detector response increases with the increase of the carrier gas flow rate [4, 5, 7, 19]. Some papers came to the conclusion that the FID response is relatively insensitive to carrier flow rate alterations [20–23]. Other sources provided information that as the carrier gas increases, the detector signal first increases and then decreases after reaching a maximum value [2, 3, 5, 6, 8].

Another crucial fact is that the majority of these measurements were carried out in the 60's which means that these data represent the level of instrumentation of that chromatographic era.

Normal alkanes are applied in many cases as reference standard both in quantitative and in qualitative measurement. For the determination of ECN values Sternberg used the n-propane and n-heptane as a reference standard first. After the introduction of the ECN method different research groups used the different normal alkanes as reference although the "equal per carbon rule" cannot be applied on any carbon number range arbitrarily. With our investigation we would like to demonstrate that even the response of the reference standard normal alkanes depends on the linear velocity. For the determination of the ECN values of the alkanes we used adjacent alkane with lower carbon number in every case. We carried out our chromatographic runs under the same chromatographic conditions, only the linear velocity was changed. With these circumstances we wanted to ensure that the detected change could be attributed solely to the change of linear velocity.

Although at higher velocities an effect could be the change in the temperature and shape of the flame. Hydrogen flame temperature can be changed with the introduction of higher flow rate carrier gas which causes an alteration in the signal production process [2].

One of the most important properties of the FID is the extreme long linear range of it. The linearity has its limitations according to studies dealing with the linear behaviour of the detector response [24–26].

The question arises as to that has an effect of carrier gas linear velocity on the carbon counting ability of the Flame Ionization Detector.

In this paper we want to investigate how the ECN value depends on the linear velocity of the carrier gas in the case of capillary columns. In the literature no data can be found on this matter. Early studies that describe the basic principles of Flame Ionization Detector show results coming from systems do not contain an analytical column or only apply a packed Gas Chromatographic column, but not capillary column [2–8].

2 Experimental

2.1 Reagents

Chemicals were analytical standards for GC from Sigma-Aldrich with a stated purity of 98 % or greater. The stock solution of normal hydrocarbons (C_{14} , C_{16} , C_{18} , C_{20} , C_{22} , C_{24} and C_{26}) in concentration of approximately 0.5 mg mL^{-1} was prepared in acetone normal hexane mixture. The working standard solution was prepared in acetone from the stock solution. Concentration levels were approximately

50 $\mu\text{g mL}^{-1}$. The declared purity was controlled, and for calculations was taken into consideration. The working standard solution was measured immediately after preparation.

2.2 Apparatus

A Shimadzu GC-2010 gas chromatograph equipped with Shimadzu AOC-20i autosampler was used. The separation was carried out by using a capillary column named BP21 (30 m \times 0.32 mm \times 0.25 μm). A single ramp (10 $^{\circ}\text{C min}^{-1}$) oven temperature program from 60 $^{\circ}\text{C}$ with no initial temperature plateau was applied. The final temperature was 240 $^{\circ}\text{C}$. The GC injector and the detector port temperature were 250 $^{\circ}\text{C}$. 1 μL was injected from each sample five times. The applied split ratio was 20:1. Nitrogen (purity 99.996 %) was used as the make-up gas with a flow rate of 30.0 mL min^{-1} . The flow rates of hydrogen (purity 99.96 %) and air were 40.0 mL min^{-1} and 400.0 mL min^{-1} , respectively. Hydrogen was used as carrier gas with linear velocity control. The observed linear velocity range was 10 cm sec^{-1} –170 cm sec^{-1} (10, 20, 30, 40, 50, 60, 80, 100, 120, 150, 170 cm sec^{-1}).

Every measuring point resulted in an average of five parallel measurements. The relative standard deviations were under 10 RSD% in every cases and under 3 RSD% for 89 % of data.

3 Results and Discussion

3.1 Effect of the linear velocity on the peak area

Our first observation was that the response of the capillary Gas Chromatographic system is different depending on the adjusted linear velocity. The raw data - even if retrieved by injecting the same working standard solution - differed in accordance with the velocity of the carrier gas (Fig. 1).

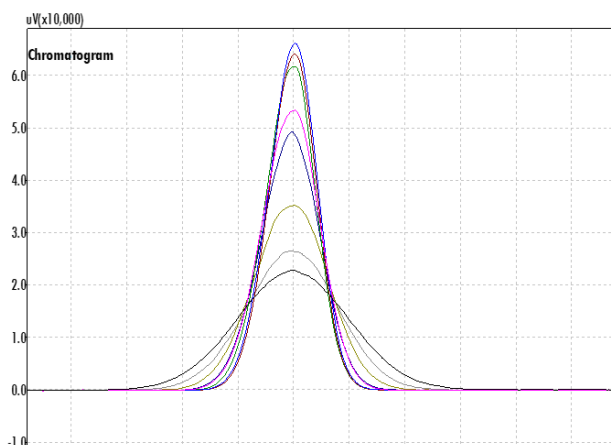


Fig. 1 Shape of the peak of normal octadecane at different linear velocity levels in the range of 10–170 cm sec^{-1} ; concentration: 60.84 $\mu\text{g mL}^{-1}$ (Peaks are aligned to the same retention interval.)

Our results show that the chromatographic sensitivity, the relation between the detector response and the injected compound weight or concentration alters for the same components depending on how fast they go through the analytical column (Fig. 2).

Area values reach the maximum value in 20–30 cm s^{-1} velocity range. Degree of deviation from the maximum area under the peak has lesser extent under 80 cm s^{-1} . Above 80 cm s^{-1} the deviation is more significant, it approaches the 30 % in some cases (Table 2) however, in the capillary Gas Chromatographic practice commonly used velocity range is 30–80 cm s^{-1} .

The effect of the increasing velocity on peak area is more significant in the case of alkanes with longer chain length.

The molar response values of the investigated seven normal alkanes illustrated on Fig. 3, in accordance with the "equal per carbon rule", the produced signal proportion to the specific carbon number. The tendency in the run of the curves is similar to Fig. 2, but the curves are shifted according to their carbon content. The molar

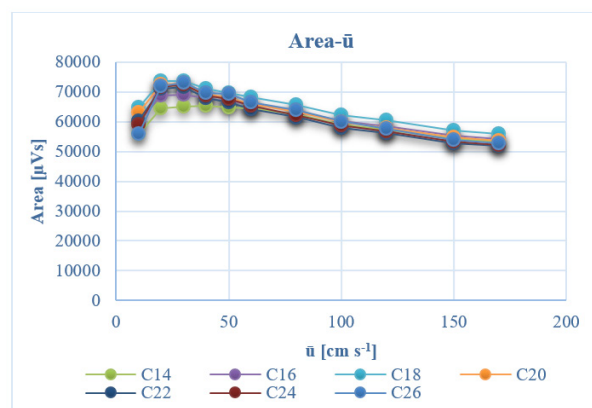


Fig. 2 Area of normal alkanes (C_{14} , C_{16} , C_{18} , C_{20} , C_{22} , C_{24} , C_{26}) at different linear velocity levels in the range of 10–170 cm sec^{-1} at 50 $\mu\text{g mL}^{-1}$ concentration.

Table 2 Area values of normal alkanes, differences according by linear velocity

	10–170 cm s^{-1}			30–80 cm s^{-1}	
	Maximum [μVs]	Minimum [μVs]	Difference, %	Minimum [μVs]	Difference, %
C_{14}	65407	53224	19	62586	4
C_{16}	69103	54227	22	63595	8
C_{18}	73771	55903	24	65628	11
C_{20}	72760	53728	26	63298	13
C_{22}	71573	51833	28	61515	14
C_{24}	72528	52257	28	62303	14
C_{26}	72995	52653	28	63925	12

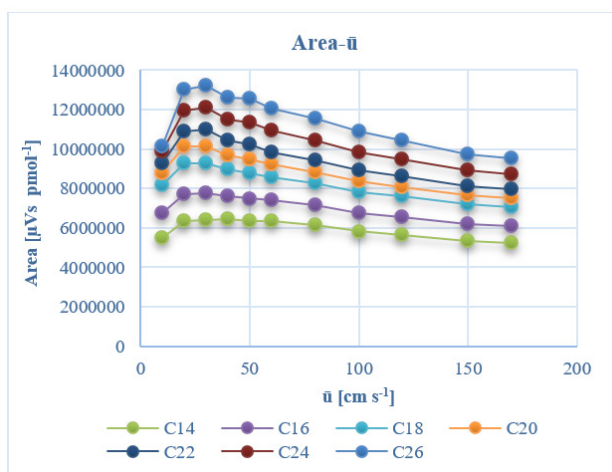


Fig. 3 The areas normalized to specific carbon number each for 1 pmol at different linear velocity levels in the range of 10–170 cm sec⁻¹

responses for each compound similarly to Fig. 3, reach a maximum in the 20–30 cm s⁻¹ velocity range and continue the run with a decrease.

Molar response values plotted as a function of carbon number for each linear velocity is shown on Fig. 4. Homologous molar responses increase linearly with the increasing of the carbon chain length. This phenomenon published by many authors [2, 15, 16] but the linear function dependency on linear velocity has not been before this paper. Raising the velocity of the carrier gas, the slope is increasing and after 30 cm s⁻¹ the slope is decreasing, and the line is flattening (Fig. 5).

The area values are smaller at very low and very high velocities than at average velocity.

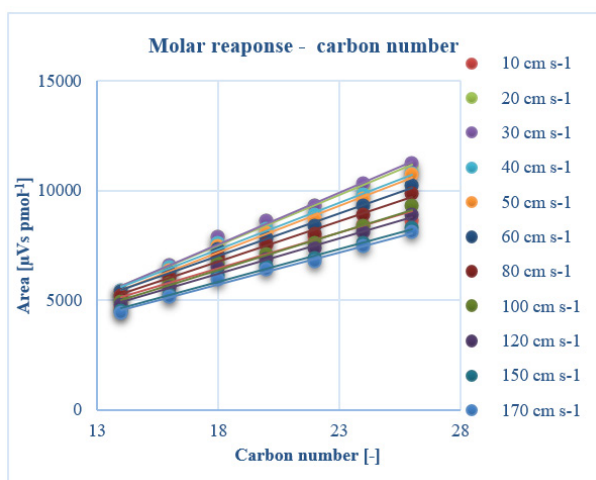


Fig. 4 Molar responses of normal alkanes (C₁₄, C₁₆, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆) displayed by carbon number

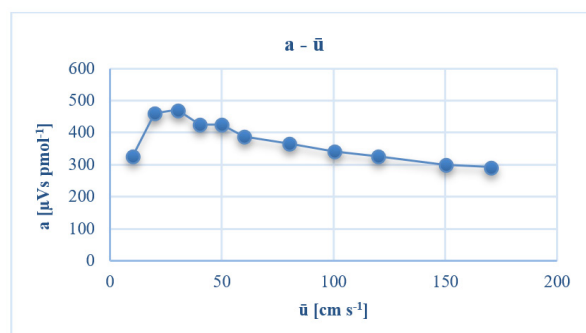


Fig. 5 The slopes of the equations displayed on Fig. 4 at different linear velocity levels in the range of 10–170 cm sec⁻¹

3.2 Effect of the linear velocity on the Effective Carbon Number

Using ECN values for the quantitative measurement connotes using a relative sensitivity. Consequently, it implies the desire that the normalized value is less affected by any chromatographic parameters. The calculated ECN values are summarized in Table 3. Our results are displayed on Fig. 6.

ECN values as a function of carbon number for each linear velocity are shown on Fig. 7. Homologous ECN values increase linearly with the increasing of carbon chain. This behaviour was observed in the 60's but the description of the linear function dependency on linear velocity is not found in the literature. Raising the velocity of the carrier gas, the slope is decreasing, the line is flattening (Fig. 8).

Comparing the slope changes of the molar responses and ECN values depending on linear velocity can be observed on Fig. 9. It seems that changes are more moderate in the case of ECNs. Using relative data after 20 cm s⁻¹ the alteration is even slighter.

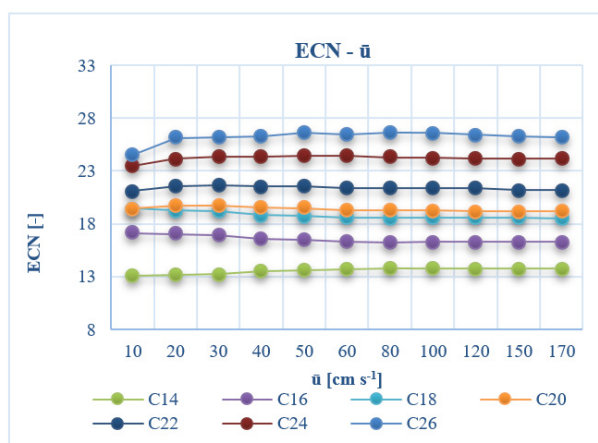
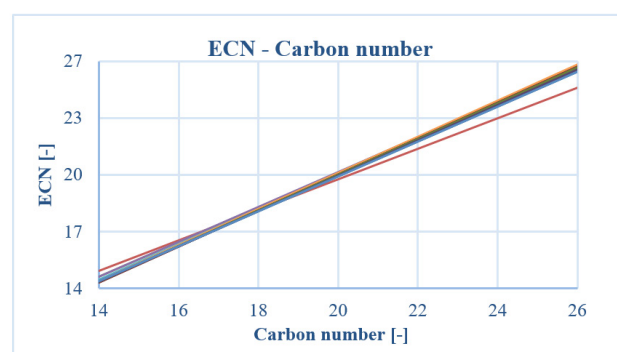
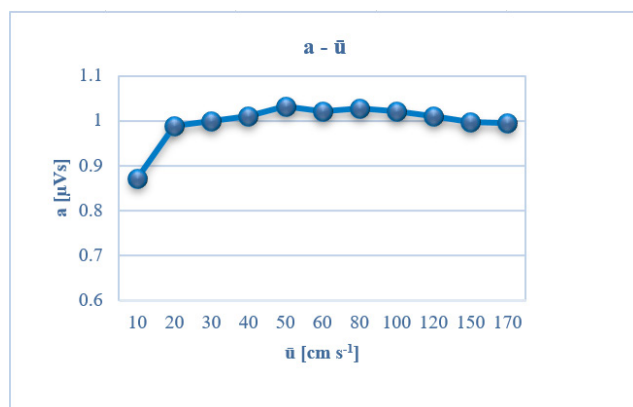
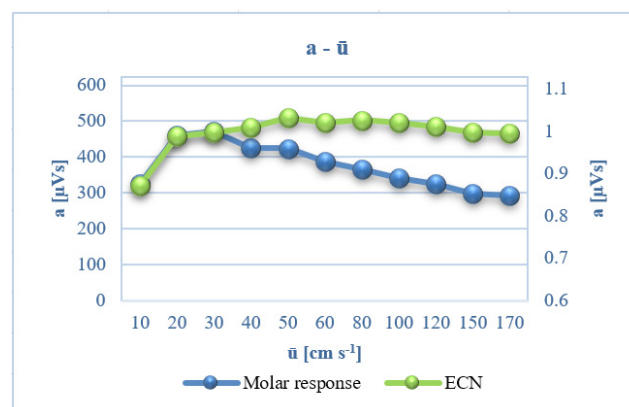
3.3 Effect of the linear velocity on the Delta Effective Carbon Number

It is an important fact that the ECN value changes by altering linear velocity. It is not negligible either that the ECN value at which linear velocity value approaches the exact carbon number best. Our results are illustrated on Fig. 10.

In the daily Gas Chromatographic practice, the linear velocity range 30–80 cm s⁻¹ has significance. Observed this range it seems that the minimum ΔECN value for alkanes with longer carbon chain length is around 80 cm s⁻¹ and for alkanes with shorter carbon chain length is around 30 cm s⁻¹.

Table 3 Effective carbon numbers at different linear velocity values in the range of 10–170 cm sec⁻¹

Linear velocity [cm s ⁻¹]	10	20	30	40	50	60	80	100	120	150	170
C ₁₄	13.1	13.2	13.2	13.5	13.6	13.7	13,8	13,8	13.7	13.8	13.8
C ₁₆	17.1	17.0	16.9	16.6	16.5	16.3	16,2	16,3	16.3	16.3	16.3
C ₁₈	19.4	19.2	19.2	18.8	18.7	18.6	18,6	18,6	18.6	18.6	18.5
C ₂₀	19.4	19.7	19.7	19.5	19.5	19.3	19,3	19,2	19.2	19.2	19.2
C ₂₂	21.1	21.5	21.6	21.5	21.6	21.4	21,4	21,3	21.4	21.2	21.2
C ₂₄	23.5	24.2	24.3	24.3	24.4	24.5	24,3	24,3	24.2	24.2	24.1
C ₂₆	24.6	26.1	26.2	26.3	26.6	26.4	26,7	26,6	26.4	26.3	26.2


Fig. 6 The ECN values at different linear velocity levels in the range of 10–170 cm sec⁻¹

Fig. 7 Effective carbon number of normal alkanes (C₁₄, C₁₆, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆) displayed by carbon number (Colour of the lines marks the same velocities as on Fig. 4.)

Fig. 8 The slopes of the equations displayed on Fig. 7 at different linear velocity levels in the range of 10–170 cm sec⁻¹

Fig. 9 The slopes of the equations displayed on Fig. 5 and Fig. 8 at different linear velocity levels in the range of 10–170 cm sec⁻¹

According to Table 4 and Fig. 10 between 50 and 60 cm s⁻¹ the velocity takes place where the difference of the highest Δ ECN value of all measured compound is the smallest. The sum of the differences is not the smallest at this velocity but the Δ ECN values are consistent for each compound. The smallest sum of Δ ECN occurs at 170 cm s⁻¹ linear velocity value.

Another interesting observation is that the sum of Δ ECN value decreases with the increasing velocity of

the carrier gas and it is less in the velocity range used in pseudo fast gas chromatography but not in the velocity range we applied under standard Gas Chromatographic circumstances, when hydrogen is the carrier gas.

4 Conclusion

For quantitative measurements it is necessary to know the dependency of the area and the derived parameters such as the molar response and the Effective Carbon Number on the different chromatographic parameters.

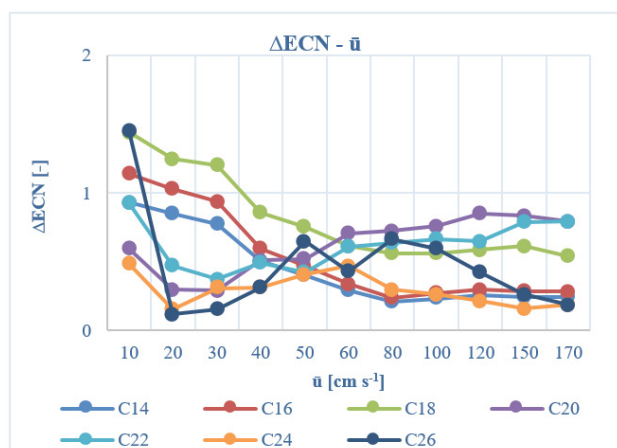


Fig. 10 Δ ECN values, differences from carbon numbers of the normal alkanes as a function of linear velocity

The effect of the linear velocity on the peak area, molar response and on the Effective Carbon Number was observed in the case of the temperature programmed capillary Gas Chromatographic separation applying Flame Ionization Detection. For our investigation we used normal alkanes (C_{14} , C_{16} , C_{18} , C_{20} , C_{22} , C_{24} , C_{26}) as model compounds.

Based on our results we have proved that the linear velocity of the carrier gas has an effect on the Flame Ionization Detector response.

Although, the Flame Ionization Detector is a mass flow rate sensitive detector, the area under the peak, molar response and ECN also show a tendency depending on the applied linear velocity value on the investigated Gas Chromatographic system. The response of the detector is not the same, even if we inject the same amount of substance into the separation system.

The effect is most significant under and above of the range of optimal linear velocities that we commonly use in the Gas Chromatographic practice.

At all the investigated compounds we observed that there is maximum response in the linear velocity range 30–80 cm s^{-1} . Above or under this velocity the response is minor.

At low linear velocities (10 cm s^{-1} –30 cm s^{-1}) the baseline width is greater than at higher velocities. In these cases, the loss upon the integration error is higher than at narrower baseline width.

There is another loss in the case of high linear velocities (80 cm s^{-1} –170 cm s^{-1}). We assume it is a result of the reduced time substances spent in the hydrogen flame, so the signal producing process cannot be completed; the production of the charged particles for the molecule is not stoichiometric. Flame capacity is exceeded in time. In this case, the carbon counting ability of the flame is retained because the sum Δ ECN values do not increase but the signal size decreases. This effect on peak area is more significant in the case of alkanes with longer chain length.

In the case of the relative response, the Effective Carbon Number the decreasing can be observed too at low linear velocities (10 cm s^{-1} –30 cm s^{-1}). At high linear velocities (80 cm s^{-1} –170 cm s^{-1}) the decreasing has lesser extent.

Investigated the Δ ECN values we came an interesting conclusion. At low linear velocities the Δ ECN values are relatively high. This range is not able to carry out a quantitative analysis with ECN method. In the 30–80 cm s^{-1} range decreasing occurs. Above the 30–80 cm s^{-1} range increasing the linear velocity the sum of Δ ECN values do not increase. The difference between the calculated ECN value and the specific carbon number for the sum of all the investigated compounds is better than at average linear velocities (30–80 cm s^{-1}). It is an incentive to use pseudo fast Gas Chromatographic circumstances in the daily Gas Chromatographic practice instead of lower linear velocities.

Table 4 Δ ECN values, differences from carbon numbers of the normal alkanes

Linear velocity [cm s^{-1}]	10	20	30	40	50	60	80	100	120	150	170
C_{14}	0.91	0.84	0.77	0.50	0.40	0.29	0.20	0.23	0.25	0.24	0.24
C_{16}	1.12	1.03	0.94	0.59	0.47	0.34	0.24	0.27	0.30	0.2810	0.2807
C_{18}	1.42	1.24	1.20	0.85	0.75	0.61	0.56	0.56	0.58	0.61	0.54
C_{20}	0.61	0.30	0.29	0.52	0.53	0.70	0.72	0.76	0.85	0.83	0.79
C_{22}	0.92	0.48	0.37	0.49	0.43	0.61	0.63	0.66	0.64	0.79	0.79
C_{24}	0.46	0.16	0.31	0.31	0.40	0.46	0.29	0.26	0.21	0.16	0.14
C_{26}	1.42	0.12	0.16	0.31	0.64	0.43	0.67	0.59	0.42	0.26	0.24
SUM Δ ECN	6.9	4.2	4.0	3.6	3.6	3.4	3.3	3.3	3.3	3.2	3.0
Average Δ ECN	1.0	0.6	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4

Minimum Δ ECN for each normal alkane in the 30–80 cm s^{-1} range are marked with italic and bold.

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