

Increasing Flame Ionization Detector Response by Silylation: The Effective Carbon Number of Carboxylic Acids

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Abstract

Detector response of carboxylic acids (C_2 – C_{12} , straight and branched chain) were investigated using a flame ionization detector (FID) in a capillary gas chromatographic system. The response of the FID for hydrocarbons is almost directly proportional to the carbon quantity introduced into the flame. Heteroatoms in the molecule reduce signal magnitude, depending on their quality and on the bond they are involved in. We expressed this reduced response with the effective carbon number (ECN). We determined the ECN contribution (Δ ECN) of the carboxyl group on the alkyl skeleton. We examined how the responses of carboxylic acids change if trimethylsilyl derivatives are evaluated and we compared the ECN of the neat and derivatized form.

Keywords

carboxylic acids, silylated derivatives, effective carbon number, flame ionization detector

1 Introduction

1.1 The FID operation principle

The capillary gas chromatography system with flame ionization detection has become a routine separation technique successfully applicable for qualitative and quantitative analysis. Relatively easy construction and maintenance, extremely wide linear range (10^7), and near-universal response for carbon-containing compounds contributed to flame ionization detector's (FID) holding such a distinguished place among the gas chromatographic detectors [1].

In the FID there is an 1500–2200 °C temperature diffusion hydrogen flame that ensures energy for converting the neutral compounds to charged particles. As a result of combustion, the analytes arriving at the detector after leaving the column with the carrier gas, transform into ions and electrons. There are two electrodes with a voltage difference, which moves around (attracts or repels) charged particles, in the presence of which current is measurable in the circuit containing the two electrodes. The radical chain mechanism that takes place in the flame also releases ions and electrons when only detector gases (hydrogen, air, make-up gas) and carrier gas are present; therefore, a low-intensity background current is detectable even if there are no analytes in the flame. However, the response

increases by orders of magnitude if carbon-containing compounds reach the flame. Signal producing mechanism starts with molecule cracking followed by pyrolysis and finally ends with ionization. In 2008, Schofield [1] in his publication summarized in detail the principles and results of the investigations in relation to the FID's operation since its invention. According to his study, in terms of electrical signal production the radical chain mechanism's key compound is the ground state CH radical which arises in quantities proportional to the carbon content [1]. This is the "one-carbon-quantum" of FID. Consequently, the resulting ions and electrons provide an electrical signal proportional to the carbon content (Eq. (1)) [1]:



To reflect this observation, it is often called a "carbon-counting detector". (One mole of octane produces very nearly the same response as two moles of butane or eight moles of methane [2].) However, this carbon-counting ability is compromised in the case of molecules containing atoms different from carbon and hydrogen. The presence of the heteroatom mostly causes a decrease in the signal since a carbon atom connected to a heteroatom cannot participate

to the fullest possible extent in signal production, although, in some cases, an increase was also observed [2].

The effort to uniformize the response of molecules containing heteroatoms appeared soon after FID began to be used. Relative responses characteristic to different compound groups have been published in the literature to quantify the response relative to different reference materials [2–15]. This classification not only accounted for the respective heteroatom that appeared in the molecule, but also the type of bond it was involved in and the molecular structure. Relative responses were defined as relative molar or relative weight responses. As reference material, mostly normal alkanes were used; however, in some cases, benzene [2, 13, 15], naphthalene [10], and even one chosen member of the investigated homologous series occurred [4, 6].

The effective carbon number as a relative molar response was introduced by Sternberg et al. [2], who published the effective carbon number (ECN) concept in his 1962 paper, which served as a basis for later ECN studies (Eq. (2)):

$$\text{ECN}_i = n_s \frac{A_i}{A_s} \frac{m_s}{m_i} \frac{M_i}{M_s} = n_s f_i \frac{M_i}{M_s}, \quad (2)$$

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

Sternberg et al. applied normal heptane and propane as a reference material [2].

The signal modifying effect caused by a specific functional group can be characterized by the ΔECN value (Eq. (3)):

$$\Delta\text{ECN}_i = \text{ECN}_i - n_i. \quad (3)$$

Table 1 lists summarized data [2, 10–15] on the characteristic ECN contribution of the carbon and heteroatoms (O, N, Cl, Br, I, Si) specified for the different functional/compound groups.

The present study focuses on the effect of oxygen on the effective carbon number.

1.2 ECN of carboxylic acids

Although several authors provide different relative response values for carboxylic acids [4–8], characteristic ΔECN data are not available in the literature, only ECN data recalculated from previously published relative response data [10]. Furthermore, the investigators published the relative response data for only a few carboxylic acids or provided summarized results originating from different

authors, consequently from different experimental conditions [4, 6, 7]. In addition, the relative responses published mostly came from a packed column gas chromatographic system [5, 6] or from a specific apparatus [3] and for the calculations, instead of alkanes, usually one of the carboxylic acids was chosen as the reference compound [4, 6].

Although Sternberg et al. [2] did not report characteristic ΔECN for carboxylic acids, he investigated the signal-modifying effect of single and double-bonded oxygen in different species. According to his experience, the signal loss caused by the oxygen for primary, secondary and tertiary alcohols is -0.6 , -0.75 , and -0.25 respectively. He observed greater signal loss at etheric oxygen and at double-bonded oxygen in aldehydes, ketones, and esters, where the oxygen eliminated the signal of one entire carbon atom [2].

His explanation for response loss is based on that CO and CO₂ are released during the cracking step from the molecules; consequently, they cannot produce CH radicals and signal [2].

During his mass spectrometric investigation focusing on the ion formation in the hydrogen flame Nicholson and Swingler [16] came to the conclusion that decreased response of oxygen-containing molecules is due to the slowness of the CH formation reaction. For these species, the reaction rate of CO and H₂CO formation is higher.

In 1962, Ettre [4] in his short communication processed and interpreted data measured by others based on new aspects. He approximated the relative responses of acetic, propionic, butyric and valeric acid with a linear relationship (Emery and Koerner [17]). However, these responses were related not to a normal alkane but to one member of the same 4-element series, the propionic acid. He established that in the case of butyric and valeric acid, the responses of isomers are higher than in the case of corresponding straight-chain fatty acids.

Ettre in his further investigation, carried out with Kabot [5] measured the four straight-chain fatty acids (C₂–C₅) on a capillary column. The molar responses calculated were in good agreement with Emery and Koerner's [17] outcomes. They extended their measurements to even more carboxylic acids (C₂–C₅, C₇, C₈, C₁₀, C₁₂). However, they were measured only on a packed column. The carbon number relative to molar response was approximated with a linear straight line. However, acetic acid and propionic acid gave notably lower responses than the line. They attributed this to the significant effect of the carboxyl group on the relatively short alkyl chain, which is weaker on longer chains. Perkins et al. [3] investigated the relative molar

Table 1 Contributions to the effective carbon number published by different authors

Atom	Type	Sternberg [2]	Scanlon and Willis [10]	Jorgensen et al. [11]	Morvai et al. [12]	Kállai et al. [13], and Kállai and Balla [14]	Mátyási et al. [15]	Recent work (2023)
C	Aliphatic	1	–	0.88	–	0.98	–	–
C	Aromatic	1	–	1.09	–	0.46/–0.12	–	–
C	Olefinic	0.95	–	–	–	–	–	–
C	Acetylenic	1.30	–	–	–	–	–	–
Cl	Chloroalkanes	–0.12 each	–	–	–	–0.55	–	–
Cl	On aromatic C	–	–	–	–	–0.14	–0.2–(–0.3)/Cl	–
Cl	On olefinic C	+0.05	–	–	–	–	–	–
Br	Bromoalkanes	–	–	–	–	–0.25	–	–
I	Iodoalkanes	–	–	–	–	–0.14	–	–
O	Primary alcohols	–0.60	–	–0.42	–	–0.72	–	–
O	Secondary alcohols	–0.75	–	–0.58	–	–	–	–
O	Tertiary alcohols	–0.25	–	–	–	–	–	–
O	Phenols	–	–	–0.83	–	–	–	–
O	Ethers	–1.0	–	–0.75*	–	–	–	–
O	Furans	–	–	–0.82	–	–	–	–
O	Aldehydes	–1.0	–	–	–	–	–	–
O	Ketones	–1.0	–	–0.80	–	–0.99	–	–
–COOH	Acids	–	–	–	–	–	–	–1.20–(–2.90)
–COOR	Esters	–1.25	–	–1.27	–	–1.49	–	–
–COOR	Esters	–	–	–	1.1/1.73/2.23/ 3.23/3.34**	–	–	–
N	Primary amines	–0.60	–	–0.58*	–	–0.79	–	–
N	Secondary amines	–0.75	–	–	–	–	–	–
N	Tertiary amines	–0.25	–	–	–	–	–	–
N	Nitriles	–0.7	–	–	–	–	–	–
N	Nitrogen heterocycles	–	–	–0.62	–	–	–	–
H–C–O–Si(CH ₃) ₃	Alcohols, TMS	–	3.69–3.78	–	–	–	–	–
–CO ₂ –Si(CH ₃) ₃	Acids, TMS	–	3.0	–	–	–	–	2.34
–CH=N–O–Si(CH ₃) ₃	Silyl oximes	–	3.3	–	–	–	–	–
–CH=N–O–CH ₃	Methoximes	–	0.92–1.04	–	–	–	–	–

* Only ethers/amines containing minimum 1 aromatic rings as substituents.

** The values are the increments of ethyl/i-propyl/n-propyl/i-butyl/n-butyl esters.

In the case of red colour marking, the provided contribution applies only to the red-marked atoms specifically only in that functional group.

responses of numerous homologous series. However, they did not provide the specific numerical values, only diagrams, based on which conclusions were drawn on the

characteristic ECN increments of the compound groups by the authors. The ECN contribution of the acids determined by the method presented was –1.

As subsequently noted by Ackman, contrary to Sternberg's results Perkins' figure showed that the signal-reducing effects of the carboxylic acids and aldehydes were different [7]. The relative molar response of aldehydes was found to be higher than acids. The difference is more significant in longer-chain acids. Ackman assumed there is a variation in the ion formation and signal production procedure between the aldehydes and acids [7].

Ackman and Sipos [6] compared his earlier published data (carboxylic acids C_2 – C_6) complemented with a few new measured values (carboxylic acids C_9 , C_{10}) to Kabot and Ettre's responses [5]. He did not experience a different behavior in the molar responses of low-chain fatty acids. Furthermore, he found that there is no significant difference between branched and straight-chain isomers' molar responses [6].

In the 80's Scanlon and Willis [10] investigated the ECN of different polycyclic aromatic hydrocarbons and oxygenated organics. They compared the neat and derivatized forms for different species, like alcohols, n-acids, carbohydrates and aromatic carbonyls. They prepared trimethylsilyl, trimethylsilyl-oxime (TMS) and methoxime derivatives. However, they did not measure ECN for neat carboxylic acids. For comparison, they used ECNs calculated based on Dietz's [8] earlier published response factors (1.01, 2.07, 2.95, 5.11, 5.55, 6.55 for acetic, propionic, butyric, hexanoic, heptanoic and octanoic acid, respectively). Scanlon and Willis determined ECN for TMS-derivatives of hexanoic, heptanoic, octanoic and nonanoic acids to be 8.00, 8.80, 9.94, and 10.83, respectively. The ECN of the whole $-\text{CO}_2-\text{Si}(\text{CH}_3)_3$ group was measured to be 3.0 [10].

In the case of alcohol's TMS-derivatives, where there is no carbonyl oxygen, they determined a higher 3.69–3.78 contribution in the case of the $\text{H}-\text{C}-\text{O}-\text{Si}(\text{CH}_3)_3$ group [10].

25 years after Sternberg's paper, Jorgensen [11] reexamined and extended his ECN data. In every case, he measured lesser ΔECN values. However, the differences were, for the most part, insignificant. The maximum deviation obtained between the two data series was for ethers, with $\Delta\text{ECN} = 0.25$. Jorgensen found the differences surprising since there have been significant changes in instrumentation in 25 years. For carboxylic acids or their TMS derivatives no data was reported [11].

In 2001 and 2002 Kállai et al. [13], and Kállai and Balla [14] published the ECN of different homologous series. These papers were the reexamination of earlier studies and at the same time they were the extension of

literature on the ECN of ketones, aromatic and halogenated compounds. Comparison of the ECN values obtained to earlier data in some cases revealed significant differences, which can be partly attributed to modern instrumentation. Although they did not investigate carboxylic acids or their TMS derivatives, in connection with the examination of esters, they stated that the ECN contribution of the OH group in a carboxyl group is different from that of the OH group in alcohol. Furthermore, the double-bonded oxygen and the hydroxyl group in the carboxyl group bonded to the same carbon atom; consequently, the ECN contribution of the carboxyl group cannot be identical with the sum of ECN increments of $=\text{O}$ and $-\text{OH}$ groups [13, 14].

1.3 ECN in practical use

These increments give an idea of the effect of the molecular structure on the FID signal, despite the fact that, as pointed out in our previous publications [18, 19] and in agreement with the experiences of other authors [9, 20], they are subject to the experimental conditions in which they take place. Although these ECN modifying constants (Table 1) are very useful when our target compound is a so-called CLASS compound (Compounds Lacking Authentic Standards or Surrogates [21]) whose FID-response can only be established by calculation based on the ECN method rather than by experimental means.

Another efficient application of ECN values is using them for column tests [10, 22]. The decreased ECN of the test compounds indicates active points on the stationary phase which cause irreversible adsorption.

The ECN loss can show the thermal decomposition of substance in the injector or the purity of the standards [10].

The ECN method is a useful tool for monitoring the efficiency of derivatization too.

1.4 Neat and derivatized form

The application of derivatization techniques is beneficial for many reasons. It provides thermal stability for compounds that would not be measurable with gas chromatography (GC) due to their thermal sensitivity. With derivatization, active hydrogens are replaced; consequently, in some cases, the boiling points will be reduced. In addition, by replacing polar groups for more apolar substituents the excess sorption on the stationary phase will be eliminated, and eluted peaks will be more symmetrical. With derivatization, the sorption difference between the analytes can be increased, resulting in improved separation [23].

[illegible]

acid. The ECN contribution of the sum of =O and –OH groups (characteristic for carboxylic acid) was measured to be in the range from –1.20 to –2.90. We observed an increasing tendency in Δ ECN as a function of the increase of carbon number, a phenomenon in accordance with other researchers' findings with other homologous series [11, 13]. Relative standard deviations (RSD%) of the five parallel measurements were under 3.0%.

The ECN loss for carboxylic acid is higher than for esters, although they also contain 2 oxygens (=O and –O–).

3.2 The effective carbon number of carboxylic acids' trimethylsilyl derivatives

ECN values of carboxylic acid were observed after the formation of their trimethylsilyl derivatives as well. The ECNs plotted against the carbon number are displayed in Fig. 2. We fitted a straight line to the data the determination coefficient of which was 0.996. In accordance with our findings with the neat acid form, we observed a slightly increasing tendency in the Δ ECN values compared to the actual carbon number (Table 2). The measured ECN loss was in the range from –1.37 to –2.11. RSD% was under 1.2% in every case.

The average ECN contribution of the whole $-\text{CO}_2-\text{Si}(\text{CH}_3)_3$ group was determined as 2.34. This value is lower than Scanlon and Willis' result (3.00) [11], although they investigated TMS derivatives in fewer numbers.

The carboxylic group in TMS derivative forms a higher ECN increment (2.34) than in *i*-propyl (1.73) or *n*-propyl (2.23) ester derivatives, despite the fact that these alkyl esters groups also contain 3 carbon atoms.

With the addition of the carbon-containing TMS group to our target compounds, increase was observed in the detector response in every case. Fig. 3 represents the responses of the neat and derivatized straight-chain carboxylic acids

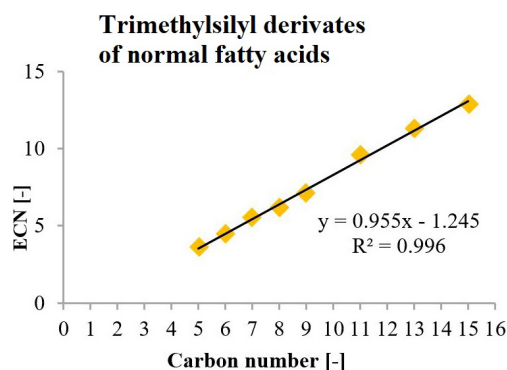


Fig. 2 Relationship of effective carbon number and actual carbon number, trimethylsilyl derivatives of straight chain fatty acid (C_2-C_{12})

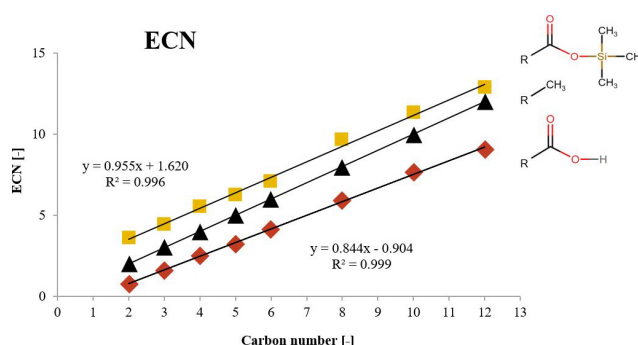


Fig. 3 Relationship of ECN and actual carbon number, red: straight chain fatty acids (C_2-C_{12}), yellow: trimethylsilyl derivatives of straight chain fatty acids (C_2-C_{12}), black: alkanes (theoretical values)

investigated in comparison. ECNs were plotted against to carbon number of the neat acid in both cases.

It is spectacular that there is an ECN gain on the detector response using TMS derivatives in comparison to the underivatized form. There is a slight tendency; the longer the chain the bigger the ECN gain.

3.3 The effective carbon number of straight and branched chain carboxylic acids and their trimethylsilyl derivatives

In the case of butyric, valeric and hexanoic acid we have also measured the ECN of their branched chain isomers. When observing the underivatized form's responses we experienced, like Ettre [4], a higher ECN for the branched chain than the straight chain acids (Fig. 4).

In the case of TMS derivatives the differences were more moderate. With the butyric and valeric acid, the ECN values were within 0.1. For hexanoic acid bigger difference was observed.

4 Conclusion

The effective carbon number of straight and branched chain carboxylic acid was determined in the C_2-C_{12} carbon atom range. We established an ECN contribution (Δ ECN) range characteristic of open-chain carboxylic acids from

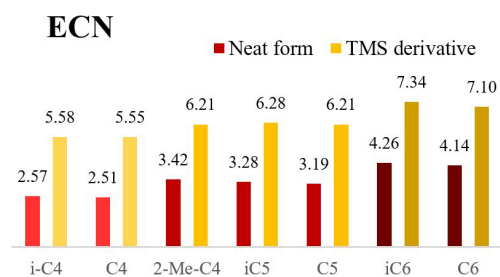


Fig. 4 ECN of carboxylic acid isomers (C_4-C_6), neat and TMS derivatized form

–1.20 to –2.90. This is a higher negative effect on response than the effect of alkyl esters. We found a linear relationship between carbon number and ECN.

We also investigated the acids' responses after replacing the active hydrogen of the carboxyl group with a trimethylsilyl group. The derivatized form produced in every case a higher molar response; the ECN gain range was 2.78–3.79 compared to the non-derivatized form. With these results, we demonstrated that the advantage of silylation, beyond the general gas chromatographic benefits earlier discussed, is its increasing effect on the detector response. In the case of silylated acids, we also observed a linear relationship between carbon number and the ECN of TMS derivatives.

We determined the ECN contribution of the whole $-\text{CO}_2-\text{Si}(\text{CH}_3)_3$ group the value of which was 2.34. Based on this finding we established that in the TMS ester group, the signal production is more efficient than in alkyl esters, which also have 3 carbon atoms (propyl and i-propyl esters).

Although the ECN depends on the experimental conditions [9, 18–20], it contributes to collecting increasingly

more information for compound classes on the nature of the processes taking place in the flame ionization detector. If we know the approximate responses of our target compounds, we can detect anomalies in our separation system, like decomposition in the injection port, excess sorption on the stationary phase, or insufficient efficiency of derivatization.

By measuring the members of a specific compound class, we can reduce the number of analytical standards to be purchased [15].

In the case of CLASS compounds, to which the silylated compounds also belong, the ECN method is the only way to determine the expected FID response, relying on the experimental molecular response data accumulated so far.

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References

- [1] 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>
- [2] Sternberg, J. C., Gallaway, W. S., Jones, D. T. L. "The mechanism of response of flame ionization detectors", In: Brenner, N., Callen, J. E., Weiss, M. D. (eds.) *Gas chromatography: Proceedings of the 3rd International Symposium*, Academic Press, New York, NY, USA, 1962, pp. 231–267.
- [3] 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: Brenner, N., Callen, J. E., Weiss, M. D. (eds.) *Gas Chromatography: Proceedings of the 3rd International Symposium*, Academic Press, New York, NY, USA, 1962, pp. 269–285.
- [4] Ettre, L. S. "Relative response of the flame ionization detector", *Journal of Chromatography A*, 8, pp. 525–530, 1962.
[https://doi.org/10.1016/S0021-9673\(01\)99303-3](https://doi.org/10.1016/S0021-9673(01)99303-3)
- [5] Kabot, F. J., Ettre, L. S. "Gas Chromatography of Free Fatty Acids III. Quantitative Aspects", *Journal of Chromatographic Science*, 1(10), pp. 7–10, 1963.
<https://doi.org/10.1093/chromsci/1.10.7>
- [6] Ackman, R. G., Sipos, J. C. "Flame Ionization Detector Response for the Carbonyl Carbon Atom in the Carboxyl Group of Fatty Acids and Esters", *Journal of Chromatography A*, 16, pp. 298–305, 1964.
[https://doi.org/10.1016/s0021-9673\(01\)82491-2](https://doi.org/10.1016/s0021-9673(01)82491-2)
- [7] Ackman, R. G. "Fundamental Groups in the Response of Flame Ionization Detectors to Oxygenated Aliphatic Hydrocarbons", *Journal of Chromatographic Science*, 2(6), pp. 173–179, 1964.
<https://doi.org/10.1093/chromsci/2.6.173>
- [8] Dietz, W. A. "Response factors for gas chromatographic analyses", *Journal of Gas Chromatographic Science*, 5(2), pp. 68–71, 1967.
<https://doi.org/10.1093/chromsci/5.2.68>
- [9] Tong, H. Y., Karasek, F. W. "Flame ionization Detector Response Factors for Compound Classes in Quantitative Analysis of Complex Organic Mixtures", *Analytical Chemistry*, 56(12), pp. 2124–2128, 1984.
<https://doi.org/10.1021/ac00276a033>
- [10] 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>
- [11] 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>
- [12] Morvai, M., Pályka, I., Molnár-Perl, I. "Flame Ionization Detector Response Factors Using the Effective Carbon Number Concept in the Quantitative Analysis of Esters", *Journal of Chromatographic Science*, 30(11), pp. 448–452, 1992.
<https://doi.org/10.1093/chromsci/30.11.448>
- [13] 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>
- [14] Kállai, M., Balla, J. "The Effect of Molecular Structure upon the Response of the Flame Ionization Detector", *Chromatographia*, 56(5), pp. 357–360, 2002.
<https://doi.org/10.1007/BF02491945>

- [15] Mátyási, J., Nyerges, G., Balla, J. "The Effective Carbon Number of Chlorobenzenes: Quantitative Determination with the CBs-ECN Method", *Periodica Polytechnica Chemical Engineering*, 2023.
<https://doi.org/10.3311/PPch.22100>
- [16] Nicholson, A. J. C., Swingle, D. L. "Ion formation in the flame ionization detector", *Combustion and Flame*, 39(1), pp. 43–52, 1980.
[https://doi.org/10.1016/0010-2180\(80\)90005-X](https://doi.org/10.1016/0010-2180(80)90005-X)
- [17] Emery, E. M., Koerner, W. E. "Gas Chromatographic Determination of Trace Amounts of the Lower Fatty Acids in Water", *Analytical Chemistry*, 33(1), pp. 146–147, 1961.
<https://doi.org/10.1021/ac60169a048>
- [18] 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>
- [19] 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>
- [20] Boček, P., Janák, J. "Flame ionisation detection: (Flame ionisation phenomena)", *Chromatographic Reviews*, 15(2–3), pp. 111–150, 1971.
[https://doi.org/10.1016/0009-5907\(71\)80016-9](https://doi.org/10.1016/0009-5907(71)80016-9)
- [21] Szulejko, J. E., Kim, K.-H. "Re-evaluation of effective carbon number (ECN) approach to predict response factors of 'compounds lacking authentic standards or surrogates' (CLASS) by thermal desorption analysis with GC-MS", *Analytica Chimica Acta*, 851, pp. 14–22, 2014.
<https://doi.org/10.1016/j.aca.2014.08.033>
- [22] Nyerges, G., Mátyási, J., Balla, J. "Comparison of 624-type Capillary Columns: "Equivalent Columns" Deviation in the Quantitative Analysis", *Periodica Polytechnica Chemical Engineering*, 2023.
<https://doi.org/10.3311/PPch.21611>
- [23] Moldoveanu, S. C., David, V. "Derivatization Methods in GC and GC/MS", In: Kusch, P. (ed.) *Gas Chromatography - Derivatization, Sample Preparation, Application*, IntechOpen, 2019, pp. 1–33. ISBN 978-1-83881-866-1
<https://doi.org/10.5772/intechopen.73339>