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The Effective Carbon Number of Chlorobenzenes

Quantitative Determination with the CBs-ECN Method

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, Szent Gellért tér 4., H-1111 Budapest, Hungary
[2] B&B Analytics Ltd., Terasz utca 60., H-2030 Érd, Hungary
[*] Corresponding author, e-mail: matyasi.judit@vbk.bme.hu

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Abstract

Detector response of 12 chlorobenzenes was investigated (mono-, di-, tri-, tetra-, penta-, and hexachlorobenzene, CBs) using flame ionization detector in a capillary gas chromatographic system. We determined the signal-reducing effect of the chlorine atom on the aromatic ring relative to the number of the chlorine substituents and expressed with the effective carbon number (ECN). Benzene was applied as a reference substance. Using the signal-modifying pattern of the chlorine atoms on the benzene's response, we developed an alternative calibration measurement method (CBs-ECN method) for the 12 CBs and compared it with classic calibration. The differences in the concentrations calculated by the two quantitative methods were under 4.5% for 11 CBs and 7% for one compound.

Taking advantage of the opportunities provided by the CBs-ECN pattern it is not necessary to apply all of the 12 CBs but only one single component, the hexachlorobenzene for the calibration. With this simplification, the preparation of the calibration standards is faster, does not require purchasing all 12 CBs for each subsequent calibration, and the exposure to harm and expenses are reduced.

Keywords

chlorobenzenes, effective carbon number, quantitative determination, flame ionization detector

1 Introduction

In the gas chromatographic field flame ionization detector (FID) is the most widely used detector. Since its invention in 1957 [1, 2], it has been used continuously and is indispensable in pharmaceutical, petrochemical, environmental, biological, and food analysis. The relatively simple instrument design, the wide linearity range, and the inexpensiveness contributed to its popularity. The soul of the apparatus is the approximately 2 mm high laminar diffusion hydrogen flame that provides a place for the radical mechanism chain reaction, which yields ions and electrons. These charged particles are attracted to either the anode or the cathode generating current in the circuit. The electrical signal is measurable with an ampere meter or a voltmeter and could be converted into analytical information.

The processes taking place in the hydrogen flame were published in detail by Schofield in 2008 [3], with a summary of the results of the studies on the subject since the beginning, and an answer to the elementary question of the *enigmatic mechanism* of the detector.

In 1962, Sternberg et al. [4] published a detailed study about the principle of the FID operation which served as the basis for many further publications. According to their observation, the response of the FID for hydrocarbons is almost directly proportional to the quantity of carbon introduced into the flame. One mole of octane produces very nearly the same response as two moles of butane or eight moles of methane. This "carbon-counting" behaviour of FID provides an opportunity to analyse a wide spectrum of organic compounds. However, this "carbon-counting" ability is modified for heteroatom-containing molecules. In the presence of oxygen, halogens or nitrogen signal loss is experienced. The contribution of carbon atoms which take part in heteroatomic bonds is less in signal production. However, the signal-modifying effect depends on the quality of the heteroatomic bond and the compound's chemical structure. For example, the oxygen in the carbonyl group of aldehydes eliminates the whole response of the carbon atom. In contrast, the presence of oxygen in tertiary alcohols reduces the signal by a mere 25%.

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The effectiveness of carbon atoms in signal production can be described with the effective carbon number (ECN) introduced by Sternberg et al. [4] in 1962 by Eq. (1):

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

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

The signal reduction caused by a given functional group can be characterized by the ΔECN value (Eq. (2)).

$$\Delta\mathrm{ECN}_i = \mathrm{ECN}_i - n_i \tag{2}$$

The characteristic ΔECN values determined for different component groups are displayed in Table 1 [4–7].

Although several authors published ECN values for aliphatic halogenated compounds, data pertaining to aromatic halogenated compounds are available to a lesser extent, and the signal-producing mechanism in the presence of halogenated compounds is not clarified in detail.

Sternberg et al. [4] in 1962 investigated the response of aliphatic chlorine-containing hydrocarbons. According to his experience, a single chlorine has a negligible effect on the molecular response. His explanation is based on the rupture of the weak carbon-chlorine bond, which results in the formation of hydrocarbon radicals in the flame, which follow the reaction pathway of simple hydrocarbons. Two or more chlorine at one carbon atom has a significant ECN-decreasing effect (−0.12 each chlorine, from the 2nd); however, chlorine captured to an olefinic carbon atom increases the ECN (+0.05). He assumed the possibility of HCl formation during the radical mechanism chain reaction in the flame (Eqs. (3)–(5)).

Table 1 ΔECN values published by different authors

Class	Sternberg et al. [4]	Jorgensen et al. [5]	Kállai et al. [6]; Kállai and Balla [7]
	Average ΔECN	Average ΔECN	Average ΔECN
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

$$\mathrm{CCl} + \mathrm{OH}^* \rightarrow \mathrm{CHO}^+ + \mathrm{Cl}^- \tag{3}$$

$$\mathrm{CCl} + \mathrm{O_2}^* \rightarrow \mathrm{CO_2}^+ + \mathrm{Cl}^- \rightarrow \mathrm{CO_2}^+ + \mathrm{Cl} + \mathrm{e}^- \tag{4}$$

$$\mathrm{CCl} + \mathrm{H_2O}^* \rightarrow \mathrm{CHO}^+ + \mathrm{HCl} + \mathrm{e}^- \tag{5}$$

Holm and Madsen [8] investigated the decomposition products of alkyl halogenates by heating the test compounds up to 1400 °C in excess hydrogen in a quartz capillary. They introduced the heated mixture into an FID. They detected hydrocarbons and hydrogen halides formed from halogenated compounds. They corroborated the detection with a mass spectrometer too. The results of a further investigation carried out by Holm [9] indicated that 1-chlorobutane shows no loss on response, after elimination of HCl, the remaining alkyl part gives the same signal as butane. Regarding the ECN of $\mathrm{CCl_4}$, he raised the possibility that carbon monoxide and/or chlorine is generated besides HCl or short-life radicals like $\mathrm{CCl_2}$ form without ion production. He attributed the ECN excess observed at trichloroethylene or tetrachloroethylene to alternative positive ion formation different from $\mathrm{CHO^+}$, but he did not propose a possible chemical structure for the ion quality. He came to the conclusion that the signal production of aromatic halogenated compounds is more complicated than aliphatic halogenated species.

During their hydrodechlorination investigation, Manion et al. [10] observed that the dechlorination of chlorobenzenes is much slower than aliphatic and olefinic chlorides in $\mathrm{H_2}$ atmosphere. Their observations were collected at quartz reactor experiments in the temperature range from 973 to 1198 K. They established that HCl is formed during the "hydrocracking".

Ritter and Bozelli [11] studied the thermal reaction of monochlorobenzene and dichlorobenzene in hydrogen and hydrogen/oxygen atmosphere. They used a tubular flow reactor for their experiments. They carried out their test in the temperature range from 833 to 1275 K at 1-atmosphere pressure. Both chlorobenzenes' major products were: benzene, carbon solids, HCl, and in lesser amounts, methane and ethane were formed. Amounting to less than 0.5%, toluene, cyclopentadiene, biphenyls, ethylene and acetylene were observed and also carbon monoxide and carbon dioxide appeared in the presence of oxygen. The initiating step of the conversion is the same for both mono- and dichlorobenzene: a dissociation of Cl and phenyl radical. Although in the case of dichlorobenzene this is slightly faster because of the weaker C-Cl bond.

Tong and Karasek [12] reported response factors (peak area counts of compound/quantity of compounds injected in ng) of 5.60, 5.08 and 4.54 for tetra-, penta- and hexachlorobenzene, respectively. The higher the number of heteroatoms the lower the response of the detector.

In our earlier studies [6, 7] we investigated the ECN of a few chlorobenzenes, but not all 12. Like Tong and Karasek [12], we also experienced that the ECN decreases with the increase of chlorine number on the benzene ring in contrast to the negligible heteroatom effect we experienced with alkyl halides. We ascribed this phenomenon to the stronger Cl-C bond compared to alkyl chlorides. The Cl atom with its lone electron pairs is bonded not only through the σ-bond to the aromatic ring but is also part of the delocalized π-electron system of the benzene. Consequently, the Cl split off with the carbon atom; therefore it could not go through the signal-producing pathway. In addition, the insufficient contact time spent in the flame can also play a role, which does not allow CB's total transformation, resulting in reduced ECN values. Our research group [13, 14] previously showed that the ECN-reducing effect depended on experimental conditions; these findings were corroborated by the work of others [12] as well. Similarly, the parameters of chromatographic separation were reported to influence specific ECN values. Conversely, the tendency of modifying effect did not appear to be altered by these factors.

The purpose of the present paper is to determine the effective carbon number of all 12 chlorobenzenes (mono-, di-, tri-, tetra-, penta-, and hexachlorobenzene), because there is no data in the literature for all 12 compounds.

After determining the ECN values, we recognized a trend that can be approximated with a linear relationship. Exploiting the opportunities provided by the trend, we want to present an alternative quantitative determination method also acceptable in terms of the classical quantitative determination methods.

The ECN concept is a tool for quantification typically workable with CLASS compounds (Compounds Lacking Authentic Standards or Surrogates [15]), but it must also be pointed out that it is also viable in cases where authentic standards are available.

2 Experimental

2.1 Reagents

The standards were purchased from Sigma-Aldrich. Approximately 20 mg of the substances was weighed into a 20 mL volumetric flask and diluted with carbon tetrachloride. 0.5 mL stock solution was added into a 5 mL measuring flask and was diluted with carbon tetrachloride (working solution). The final concentration was around 100 µg mL^{-1} for each analyte. We analyzed the test solution immediately after preparation. Five parallel measurements were carried out.

2.2 Experimental conditions

A Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20i autosampler was used. The column was a Zebron ZB-35HT (30 m × 0.32 mm × 0.25 µm, maximum operating temperature: 400 °C). The highest boiling test component was hexachlorobenzene at 325 °C. It was important to use a column with a high maximum operating temperature to eliminate the evaporation loss in the injection port. The column temperature program started at 30 °C, then programmed to 125 °C at a rate of 5 °C min^{-1}, then programmed to 275 °C at a rate of 20 °C min^{-1}. The GC injector and the detector temperature were 390 °C and 395 °C, respectively. We injected 1 µL from each vial. Detector gases were: hydrogen 40 mL min^{-1}, air 400 mL min^{-1} and nitrogen (make-up gas) 30 mL min^{-1}. Hydrogen was used as the carrier gas in linear velocity control mode, applied value was 60.1 cm s^{-1}. The split ratio was 50:1. Before use we silylated the liner to eliminate excess sorption in the injection port.

3 Results and discussion

3.1 Determination of ECN value of chlorobenzenes

We carried out 5 parallel measurements from the working solution containing 12 chlorobenzenes and benzene as a reference component. The relative standard deviation of areas was <1.0% in the case of six compounds and did not reach 2.6% for any of the analytes. Fig. 1 represents the chromatogram of the test mixture. For the calculations, we applied Eq. (1) and Eq. (2). Table 2 lists the resulting ECN and ΔECN values for the 12 CBs.

In accordance with our previous measurements, the more chlorine substituents appear on the aromatic ring, the greater signal reduction can be measured. The magnitude of the signal loss in the presence of 5 and 6 Cl atoms already exceeds the signal corresponding to 1 full carbon atom.

It is noteworthy that the ECN value of the isomers is not the same. We found that even in the case of di, tri, and tetra isomers, the highest signal production appears in the species where the chlorine atoms are all on adjacent carbons.

It is spectacular that, compared to aliphatic chlorides, where chlorine's signal-modifying effect is negligible, a significant signal reduction occurs in the case of aromatic chlorides.

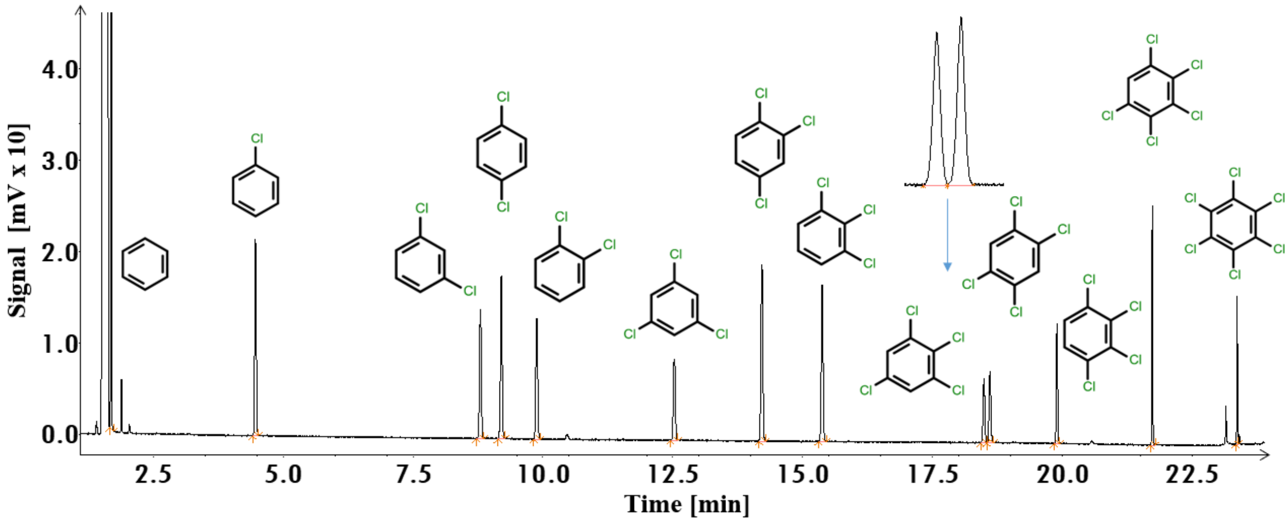


Fig. 1 Chromatogram of benzene and 12 CBs

Table 2 Measured ECN and ΔECN values for 12 CBs

	ECN	RSD%	ΔECN	ECN average	ΔECN average
Chlorobenzene	5.7	0.6	0.3	5.7	0.3
1,3-Dichlorobenzene	5.5	1.1	0.5		
1,4-Dichlorobenzene	5.6	0.5	0.4	5.6	0.4
1,2-Dichlorobenzene	5.6	1.1	0.4		
1,3,5-Trichlorobenzene	5.4	1.4	0.6		
1,2,4-Trichlorobenzene	5.2	0.8	0.8	5.4	0.6
1,2,3-Trichlorobenzene	5.6	0.8	0.4		
1,2,3,5-Tetrachlorobenzene	5.1	0.6	0.9		
1,2,4,5-Tetrachlorobenzene	5.2	0.8	0.8	5.2	0.8
1,2,3,4-Tetrachlorobenzene	5.2	1.5	0.8		
Pentachlorobenzene	4.8	1.8	1.2	4.8	1.2
Hexachlorobenzene	4.3	2.6	1.7	4.3	1.7

3.2 Pattern in chlorobenzenes ECN values

The ECN value of the CBs shows a continuously decreasing tendency with the appearance of every new chlorine atom on the aromatic ring. One new chlorine atom appearance on benzene manifests as 0.12–0.51 ECN decrease. The reference substance was benzene, which was considered to have an ECN of 6. The differences from the aromatic ring's ECN value of 6 for the certain CB can be seen in Fig. 2, where we displayed the average values for isomeric compounds.

One of the purposes of papers dealing with the determination ECN values of different compound classes is establishing whether there is a pattern in ECN values of the species of compound classes corresponding to their actual carbon number. In our case, all the investigated species had the same carbon number, 6; consequently, we could not apply this method. Instead, we plotted both the ECN and the actual carbon numbers relative to the molar mass. The outcome is given in Fig. 3. We approximated the dependence with a linear relationship. The determination coefficient of the fitted line was obtained at 0.999.

3.3 CBs-ECN method, alternative quantitative analysis

Based on the relationship shown in Fig. 3, which creates a connection between the detector responses of the different chlorobenzenes, we find that the detector responses of

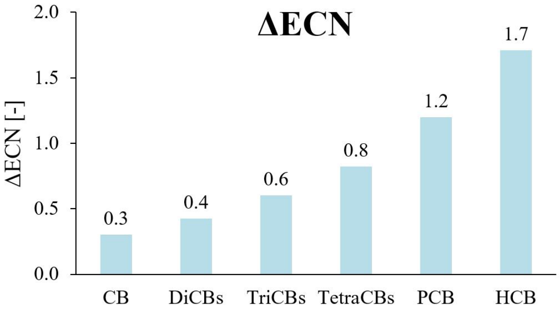


Fig. 2 Measured ΔECN values of the 12 CBs

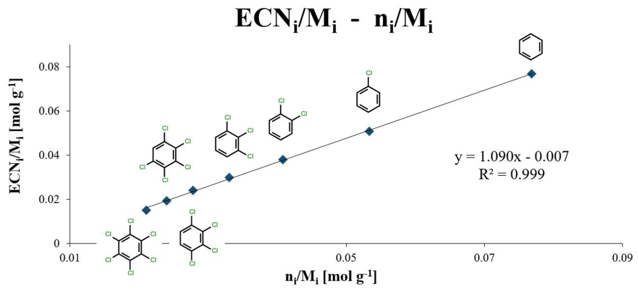


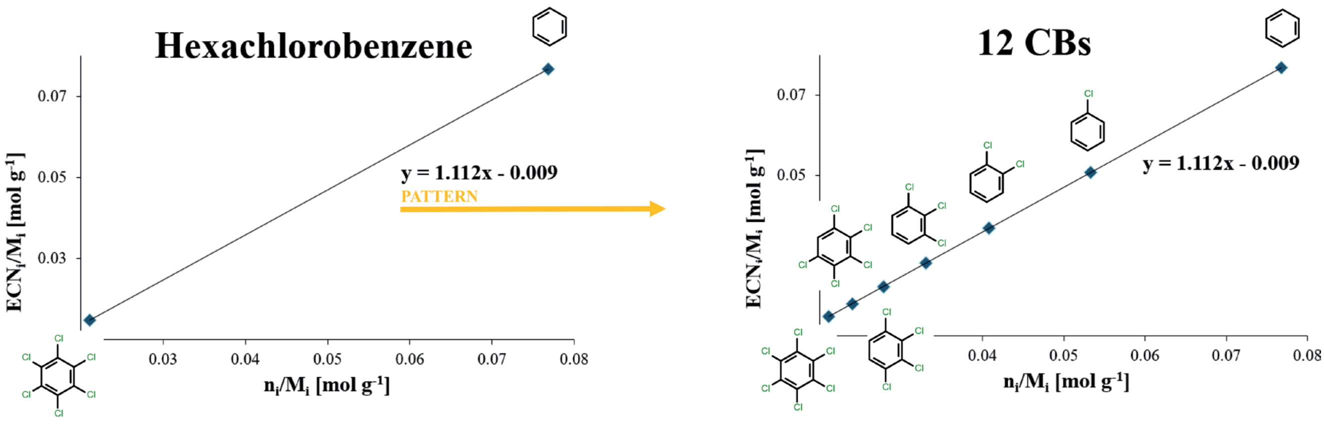
Fig. 3 Measured ECN values relative to the molar mass as a function of carbon number relative to the molar mass. In the case of isomers, the displayed value is an average value.

mono-, di-, tri-, tetrachlorobenzenes and pentachlorobenzene fall on the straight line stretching between hexachlorobenzene and benzene. We have come to the conclusion that it would be beneficial to use a modified calibration method, in which the calibration solutions contain only hexachlorobenzene and benzene as a reference instead of the 12 chlorobenzenes at different concentration levels. The FID response (ECN_i/M_i) of the other components not included in the calibration solution would be determined by the equation of the straight line determined by the response of hexachlorobenzene and benzene. Knowing the ECN_i/M_i values for each CBs, the concentration of the 12 chlorobenzenes in the unknown sample can be calculated using Eq. (1). Only benzene should be added to the sample before injecting.

Since the ECN value, which represents a relative molecular response, is a molecular property, it is not necessary to measure all 12 CBs when applying the CBs-ECN method, as the relative tendency remains unchanged. Since however, the specific ECN value depends on the experimental conditions, we have to test our measuring system with benzene and hexachlorobenzene. By injecting benzene, we obtain the characteristic response of the GC-FID system for aromatic carbon and by injecting hexachlorobenzene we obtain the characteristic response for aromatic chlorine.

The successive steps of the CBs-ECN method are illustrated in Fig. 4.

We have prepared calibration solutions from the stock solution at 3 concentration levels: 100, 200, and 350 µg mL^{-1} and injected them 3 times into the GC apparatus. (The applied concentration range should be covered the sample concentration range.) We have calculated the ECN_i/M_i values for each concentration level for benzene and hexachlorobenzene and fitted a curve to the average (Fig. 4, top left).



	c [µg mL^{-1}]					
	Sample 1	Sample 2	Sample 3	Average	SD	RSD%
Chlorobenzene	189	186	186	187	2	1
1,3-Dichlorobenzene	195	191	192	192	3	1
1,4-Dichlorobenzene	242	237	237	239	3	1
1,2-Dichlorobenzene	197	192	192	194	3	2
1,3,5-Trichlorobenzene	175	171	171	173	2	1
1,2,4-Trichlorobenzene	346	339	339	341	4	1
1,2,3-Trichlorobenzene	329	321	322	324	4	1
1,2,3,5-Tetrachlorobenzene	160	155	154	157	3	2
1,2,4,5-Tetrachlorobenzene	176	172	169	172	4	2
1,2,3,4-Tetrachlorobenzene	214	205	207	209	5	2
Pentachlorobenzene	313	299	300	304	8	3
Hexachlorobenzene	181	169	172	174	6	3

	ECN
Chlorobenzene	**5.7**
1,3-Dichlorobenzene	**5.4**
1,4-Dichlorobenzene	**5.4**
1,2-Dichlorobenzene	**5.4**
1,3,5-Trichlorobenzene	**5.1**
1,2,4-Trichlorobenzene	**5.1**
1,2,3-Trichlorobenzene	**5.1**
1,2,3,5-Tetrachlorobenzene	**4.8**
1,2,4,5-Tetrachlorobenzene	**4.8**
1,2,3,4-Tetrachlorobenzene	**4.8**
Pentachlorobenzene	**4.5**
Hexachlorobenzene	**4.2**

ECN values of CBs, currently measured for actual quantitative measurement.

Fig. 4 The successive phases of the CBs-ECN method

The equation of the line of Fig. 4 obtained is $Y = 1.112x - 0.009$. With this equation, we have calculated the actual ECN_i values for the 12 CBs. Results can be found in Fig. 4 (bottom right).

An artificial sample containing all of the CBs and benzene was injected 3 times. Substituting the measured areas in the sample chromatogram and the calculated actual ECN values into Eq. (1) we obtained the concentrations of the 12 CBs in the sample displayed in Fig. 4 (bottom left).

The concentration results compared to theoretical values show that for 6 compounds the difference is under 3.5%. For the other 6 compounds, the difference takes a value of 5.1–8.9% (Table 3).

3.4 Comparison with classic calibration

To vindicate the CBs-ECN method, we compared our results with concentration values originating from a classic 3-point calibration quantification of the artificial sample. For determination, we used nominally 100, 200, and 350 µg mL^{-1} calibration solutions, containing the 12 CBs. The outcomes compared with results from the CBs-ECN method are summarized in Table 3. Based on the results, it can be concluded that the concentrations of the CBs-ECN method do not differ significantly from the values calculated by calibration. The differences were under 4.5% for 11 CBs. However, in one case, it was 7% for 1,2,3-trichlorobenzene.

4 Conclusion

In our paper, the response of the flame ionization detector was investigated for all the 12 chlorobenzenes. We determined the signal-reducing effect of the chlorine atom (ΔECN) on the aromatic ring relative to the number of the substituents and expressed the response with the effective carbon number. No ECN data could be found in the literature for all 12 chlorobenzenes until now.

We observed a monotone response decrease with the increase in the number of chlorine atoms on the aromatic ring. The contribution of 1 additional chlorine to the ECN value was between −0.12 and −0.51. Based on these results we established that for aromatic compounds 1 chlorine connected to a carbon atom has a significant effect on ECN in contrast to alkyl chlorides, in which case chlorine has a negligible effect.

We approached the pattern of CBs' ECN values with a linear relationship. The determination coefficient of the fitted line was $R^2 = 0.999$.

Bearing in mind the signal-modifying pattern of the chlorine atoms on the benzene's response, we developed a quantitative measurement method for the 12 CBs, called CBs-ECN method. This method does not require a 12-component calibration, because the calibration solutions contain only hexachlorobenzene in addition to the reference benzene.

We tested the new method by measuring an artificial sample containing all 12 CBs. We compared the obtained results obtained with outcomes determined with a classic 3-point calibration method. The differences were under 4.5% for 11 CBs. Only in one case was it 7%: for 1,2,3-trichlorobenzene.

The ECN method is used in cases where it is not possible to obtain an authentic standard (CLASS compounds), and it is necessary to use a non-traditional quantification method.

With our measurements we demonstrated that in specific cases, it is worth carrying out quantitative determinations

Table 3 Comparison of concentrations measured by calibration and ECN method

	Concentration [µg mL^{-1}]			Difference [%]		
	Theoretical	Measured		From theoretical value		Between calibration and CBs-ECN
		Calibration	CBs-ECN	Calibration	CBs-ECN	
CB	190	192	187	1	1	0
1,3-DCB	191	194	192	2	1	1
1,4-DCB	234	237	239	1	2	1
1,2-DCB	188	191	194	2	3	2
1,3,5-TriCB	164	168	173	2	5	3
1,2,4-TriCB	341	347	341	2	0	2
1,2,3-TriCB	298	304	324	2	9	7
1,2,3,5-TetraCB	148	153	157	3	6	3
1,2,4,5-TetraCB	161	166	172	3	7	4
1,2,3,4-TetraCB	194	200	209	3	7	4
PCB	284	292	304	3	7	4
HCB	169	175	174	4	3	1

for groups of compounds too where an analytical standard would be easily available.

However, for its implementation, the knowledge of the relationship between the FID responses and the molecular structure is indispensable.

The demonstrated alternative quantification method allows the use of fewer chemicals for the analysis resulting in cost-effectiveness, lower pollution, and reduced exposure during sample preparation.

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