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Some Aspects of the Use of Carbon Dioxide as a Carrier and Makeup Gas in GC–FID Analysis

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Abstract: The paper presents the possibility of using carbon dioxide as a carrier gas in capillary gas chromatography (with a stationary liquid phase) to analyze semi-volatile compounds (boiling points of up to 400 °C). Based on the experiments carried out for compounds from the group of organochlorine pesticides (OCPs), organophosphate pesticides (OPPs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), the maximum volumetric flow rate (2.4 mL/min for CO_2) was determined, enabling the correct separation of the tested standard mixtures (except for two compounds from the OCP group: 4,4′-DDD and Endrin aldehyde and two other pairs of compounds with Rs slightly less than 1.5). Compared to using helium as a carrier gas (and makeup), carbon dioxide produces wider (about 1.6 times) and lower (about 1.8 times) peaks of analytes; these values can vary depending on the separation efficiency of the column. Carbon dioxide can also be effectively used as a makeup gas for the FID detector. The signal increase is comparable to that obtained with helium used as makeup (on average 40–50% depending on the carrier gas). When high sensitivity and high resolution are not required, CO_2 can be an alternative carrier and makeup gas to helium under the same flow conditions. The paper also describes practical aspects related to the implementation of CO_2 as a carrier and makeup gas in GC.

Keywords: carbon dioxide as a carrier gas; carbon dioxide as makeup gas; pesticide analysis; PAH analysis; PCB analysis; gas chromatography–flame ionization detector

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1. Introduction

Despite the increase in a number of mass spectrometry-based detection methods, the last decade has seen the development of studies that still use the flame ionization detector (FID) to determine compounds such as PAHs [1–5], pesticides [6–13], and PCBs [14]. This is due to the characteristics of this detector, such as a wide linear range, high sensitivity, as well as the ability to perform a rough quantitative analysis without the need for standards [15,16]. For the reasons mentioned above, it is used for quantitative analysis, often parallel to the mass detector, in both one-dimensional [17,18] and two-dimensional gas chromatography [19].

In gas chromatography, helium has been the most commonly used carrier gas for years [20]. It is also used as a makeup gas in various detectors, including FID [21]. Due to the emerging announcements about the limited availability of helium (it is a non-renewable gas) and its high prices, an intensive search for alternative carrier gases has been observed in recent years [22–25]. A gas with similar properties to helium is hydrogen, which is interchangeably used as a carrier gas [24,26,27]. However, its use is associated with increased care to avoid leaks due to the risk of explosion.

Nitrogen [21,23] is also used as a carrier gas, e.g., for the analysis of petroleum biomarkers [23], VOCs and phthalate esters [24], mineral oil hydrocarbons [28], as well as makeup for the FID detector [21]. Examples of applications using nitrogen as a carrier gas in GC are presented in Table S1 [23,24,26,28–32]. In these studies, a 30 m × 0.25 mm × 0.25 µm

column with a nonpolar stationary phase was most commonly used. Obtaining a similar resolution with nitrogen as with helium is associated with the use of much lower carrier gas flows, which results directly from the van Deemter curve [33]. When nitrogen is used as the carrier gas, lower sensitivity is also achieved [23,24,26].

A computer program such as method translation software [24,27] can be used to change the chromatograph conditions from helium to another carrier gas. Moreover, the computer software for GC operation usually allows one to select different gases used as carriers (usually: He, H_2, N_2, Ar/Me) and makeup (He, N_2). In such a situation, working with a carrier gas other than helium does not cause major problems in setting up the apparatus.

Among the gases used as makeup in the FID detector, nitrogen and helium are most often mentioned. The role of the makeup gas is to sweep components through a detector and thus cause minimization of band broadening and sensitivity enhancement. Nitrogen "better defines the shape of flame in FID" [21] compared to helium and its use is generally recommended, also in terms of its cost and availability [25]. However, helium is also used for this purpose due to the simplification of the gas installation (one gas as a carrier and makeup) [21].

Carbon dioxide is an easily available gas, as it is used in many fields—from welding to food applications. Thus, its availability is high and its price is relatively low. CO_2 as a carrier gas is used extremely rarely in GC [20], and its use as a makeup gas—to the author's knowledge—has not yet been described in the literature so far. In recent years, it has been used as a carrier gas in gas-solid chromatography with FID and TCD detectors, mainly for the analysis of hydrocarbons [34–36]. In 1991, Maeda et al. described the use of CO_2 in capillary GC with a polysiloxane column (wall-coated open tubular: WCOT column) and an FID detector [32]. For volatile analytes (C3–C5 hydrocarbons), it was found that this gas can be used as an alternative to helium at flow rates of up to 2 mL/min. The authors determined the course of the van Deemter curve for a capillary column of 30 m $\times$ 0.25 mm using hexadecane. In addition, attention was paid to the ease of CO_2 use in portable devices, due to its state of matter (liquid) in the cylinder, and thus a greater capacity compared to compressed gases (i.e., not liquefied: He, H_2). When considering the safety of working with high-pressure cylinders, it is worth mentioning that the pressure in a CO_2 cylinder at 25 °C is about three times lower (6.5×10^3 kPa, due to the liquid phase) than in a full helium cylinder (2×10^4 kPa). However, a consequence of liquefied CO_2 in the cylinder is the possibility of the valve freezing if the cylinder is not used vertically.

The purity of commercially available gases and their price are also important. Due to the degradation of the stationary phase, especially at high temperatures, the carrier gas should be free of oxygen and moisture [37]. In the case of helium 5.0, the maximum declared oxygen content is 2 ppm, and for CO_2 4.5: 15 ppm (for food grade CO_2 as much as 40 ppm). For this reason, filters (traps) are used to remove these components from the gases. In the case of the FID detector, the content of hydrocarbons is also relevant: their elevated concentration will increase noise/raise the baseline. This detector does not generate a response to the presence of water, oxygen and, above all, CO_2 [38]. The price of carbon dioxide 4.5 is several times lower than that of helium 5.0, but it can be expected that gas filters will be saturated faster (assuming the maximum declared concentration of contaminants is real).

As already mentioned, information on the usefulness of carbon dioxide in capillary gas chromatography with the WCOT column is scarce and limited to volatile organic compounds. No studies on semi-volatile (boiling points of up to 400 °C) by GC–FID using CO_2 as a carrier gas were found in the literature. Similarly, there is a lack of data on the use of this gas as a makeup gas with an FID detector.

The aim of the study was to evaluate the usefulness of carbon dioxide—used as a carrier gas in a capillary GC with a nonpolar liquid stationary phase column—for the analysis of semi-volatile organic pollutants from the group of pesticides, PAHs and PCBs. Chromatograms obtained for helium and CO_2 at a carrier gas velocity U = 45 cm/s (volume

flow rate: Q = 2.4 mL/min for CO_2) were compared. The possibility of using CO_2 as a makeup gas in the FID detector was also evaluated.

2. Materials and Methods

2.1. Chemicals

Compounds defined as environmental pollutants with boiling points (BP) of up to approximately 400 °C were used in the experiments. Standards of organophosphorus pesticides (OPPs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) at a concentration of 2000 µg/mL and polychlorinated biphenyls (PCBs) at a concentration of 10 µg/mL (all from Sigma- Aldrich, St. Louis, MO, USA) were diluted with dichloromethane (from Honeywell, Seelze, Germany) to a working concentration of 5 µg/mL, respectively. The list of substances used in the experiments is given in the description of Figure 1 and Table S2.

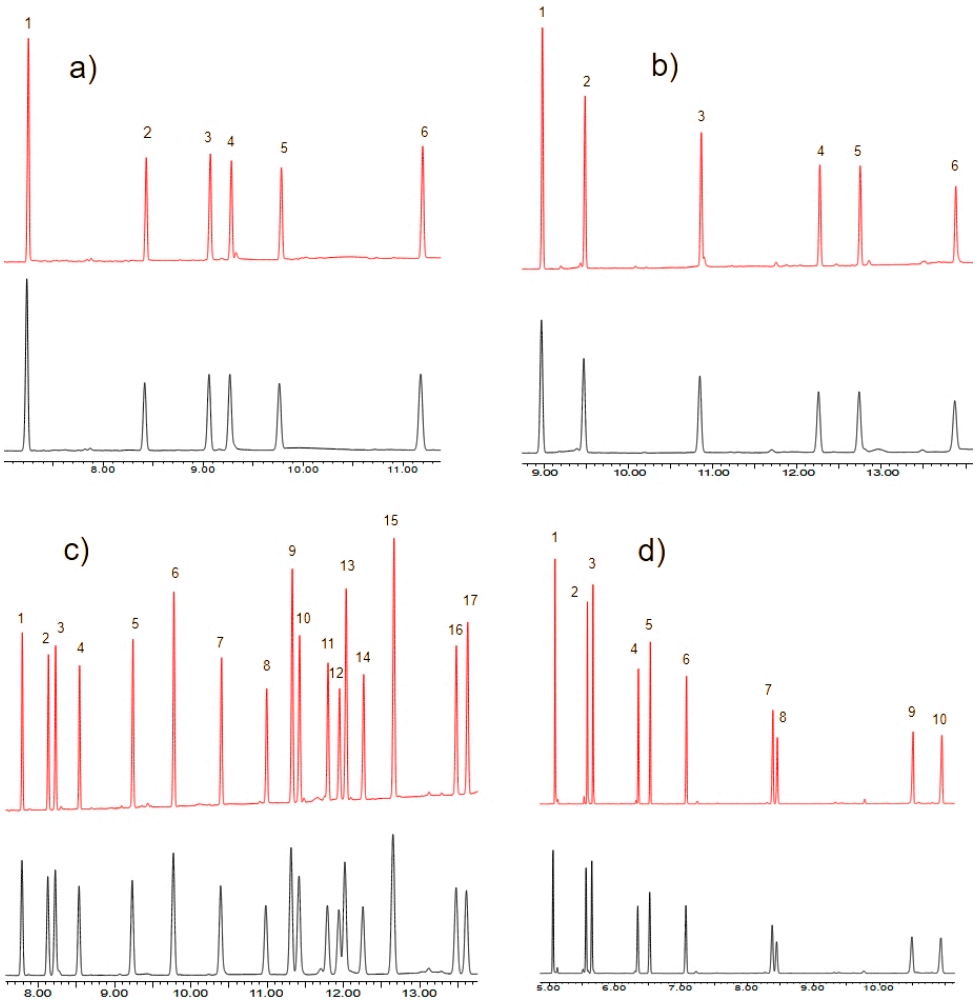


Figure 1. Chromatograms obtained as a result of experiments A (with carbon dioxide: black) and B (with helium: red) for standard mixtures of (**a**) organophosphate pesticides (1. Ethoprophos, 2. Disulfoton, 3. Parathion-methyl, 4. Fenchlorphos, 5. Chlorpyrifos, 6. Prothiofos), (**b**) polychlorinated biphenyls (1. PCB 10, 2. PCB 28, 3. PCB 52, 4. PCB 153, 5. PCB 137, 6. PCB 180), (**c**) organochlorine pesticides (1. α-BCH, 2. β-BCH, 3. γ-BHC, 4. δ-BHC, 5. Heptachlor, 6. Aldrin, 7. Heptachlor epoxide, 8. α-endosulfan, 9. 4,4′-DDE, 10. Dieldrin, 11. Endrin, 12. 4,4′-DDD, 13. Endrin aldehyde, 14. 4,4′-DDT, 15. Endosulfan sulfate, 16. Endrin ketone, 17. Methoxychlor), (**d**) polycyclic aromatic hydrocarbons (1. Naphthalene, 2. 2-methylnaphthalene, 3. 1-methylnaphthalene, 4. Acenaphthylene, 5. Acenaphthene, 6. Fluorene, 7. Phenanthrene, 8. Anthracene, 9. Fluoranthene, 10. Pyrene).

2.2. Instruments

GC–FID analyses were performed using the Agilent 7890B gas chromatograph (Agilent, Santa Clara, CA, USA) with an FID detector. A capillary column (new, used for the first time for these experiments–column 1) Rtx-5 MS (Restek, Bellfonte, PA, USA) was used for all experiments unless otherwise stated. Additionally, for some experiments, a column with an analogous stationary phase used for many weeks for the analysis of real samples (column 2) was used. The column dimensions were as follows: 30 m × 0.25 mm × 0.25 µm. Helium (purity 5.0) and carbon dioxide (purity 4.5) were used as carrier gases, with oxygen and moisture traps installed. The experiments were carried out with a carrier gas velocity U = 45 cm/s (volume flow rate: Q = 2.4 mL/min for CO_2). Additional analyses were also performed for CO_2 volumetric flow rates in the range of 0.15–2.9 mL/min. The following oven temperature program was used: 50 °C (1.5 min), 35 °C/min to 180 °C and 10 °C/min to 270 °C (1 min). Flows to the FID detector operating at 270 °C were set as follows: air 400 mL/min, hydrogen 40 mL/min, makeup 32 mL/min [39]. A volume of 3 µL of a 5 µg/mL mixture of standards was injected in the pressure-pulsed splitless injection mode of the split/splitless injector. ChemStation software (ver. F.01.03, Agilent, Santa Clara, CA, USA) was used for data acquisition and processing.

2.3. Signal Comparison for Analyses Using Helium and Carbon Dioxide

Table 1 shows the experimental conditions for helium and carbon dioxide used as carrier and makeup gas.

Table 1. List of experiments for helium and carbon dioxide (n = 5).

Experiment	A	B	C	D	E	F	G	H
carrier gas	CO_2	He	He	He	He	CO_2	CO_2	CO_2
makeup gas	CO_2	He	–	CO_2	He	–	CO_2	He
analytes	OCPs, OPPs, PAHs, PCBs					OCPs		

Experiments A and B correspond to the situation when only one gas is supplied to the GC: helium or carbon dioxide (not counting hydrogen and air needed for FID operation). These experiments aimed to compare the signal in the case of a change of carrier gas: from helium to CO_2–used for both purposes (carrier and makeup), which would occur in a situation where it is not possible to use helium (lack of it, high price or in the case of use in a portable instrument). Since the makeup gas is usually supplied to the FID detector, the same gas as the carrier gas is used in these experiments.

Experiments C to H concern evaluating the chromatographic signal in the case of using helium or carbon dioxide as the makeup gas. GC–FID analyses of the OCP standard mixture were performed using helium as the carrier gas (experiments C to E) and carbon dioxide (experiments F to H). Analyses were carried out under different conditions of makeup gas flow (CO_2 or He) and its absence. The F-Snedecor and t-Student tests were used to determine statistically significant differences for peak height and width (experiments A, B) using the built-in Data Analysis extension of MS Excel 365 (Microsoft Co., Ltd., Redmont, WA, USA). The peak heights in experiments C-H were compared using ANOVA and Tukey's test with KyPlot software ver. 6.0.2 (KyensLab Inc., Tokyo, Japan). In all cases, the significance level of $\alpha = 0.05$ was assumed.

3. Results

3.1. Practical Aspects of the Use of CO_2 in GC

Because in the case of GC–FID, the instrument was operated outside the original equipment manufacturer's specification, some of the operating parameters had to be set using a trial-and-error method. The list of carrier gases available in the GC software menu does not include CO_2. It was also impossible to control the pressure using Electronic Pressure Control (EPC) when helium was selected as the carrier gas in the software menu, and CO_2

was supplied (message displayed: Front Inlet Pressure Shutdown). After changing the carrier gas in the ChemStation software to Ar/Methane or N_2, there were no problems with the pressure control. Carrier gas velocities for CO_2 were determined experimentally based on dead (holdup) time measurements (methane retention time), at an oven temperature of 50 °C. Carbon dioxide volumetric flow rate measurements used as a carrier and makeup gas were made using a bubble flowmeter. It was found that the setting of 32 mL/min (in the EPC settings for N_2) gives a slightly higher flow, i.e., about 35 mL/min.

3.2. Signal Comparison for Analysis Using CO_2 and He

Figure 1 shows chromatograms for mixtures of pesticides, PAHs and PCBs obtained from experiments A and B. The chromatograms (in red) located at the top of the figures were obtained for helium as the carrier gas (and makeup), while those at the bottom (in black) were obtained for CO_2.

Despite working in conditions different from the flow in which the lowest theoretical plate is achieved for CO_2 [32], for almost all analyzed compounds, their correct separation (Rs ≈ 1.5) can be observed (Table S2a–d) at a carrier gas volumetric flow rate of 2.4 mL/min (45 cm/s). However, in the case of two substances from the OCP group (4,4′-DDD, Endrin aldehyde) with similar retention times, changing the carrier gas from helium to CO_2 leads to a noticeable incomplete separation (Rs = 1.11)—Figure 1c, compounds 12 and 13 and Table S2c. A separation close to Rs = 1.5 was observed for compounds such as 4,4′-DDE and Dieldrin (Rs = 1.41: Table S2c) and Phenanthrene and Anthracene (Rs = 1.31: Table S2d). Based on additional measurements performed for CO_2 flows in the range of 0.15–2.9 mL/min, it was found that complete separation of the compounds mentioned above from the OCP mixture was obtained at flows in the range of about 0.4 mL/min (minimum on the Golay curve, Figure S1). Figure S2 shows the chromatogram for the tested flow rates: 0.15 mL/min (complete separation achieved) and 2.9 mL/min (co-elution of some compounds). Increasing the volumetric flow rate of CO_2 to 2.9 mL/min resulted in increased incomplete separation between compounds 9 and 10 (4,4′-DDE, Dieldrin) from the OCP group (Figure S2). Thus, the volumetric flow rate of the carrier gas (CO_2) equal to 2.4 mL/min in experiments (A to H) seems to be an acceptable compromise between the analysis time and the obtained resolution. The Golay curves for α-BHC (BP = 323 °C) and Aldrin (BP = 330 °C) are shown in Figure S1; their course is similar to the one published for Hexadecane (BP = 287 °C) [32].

When comparing the chromatograms, the peak height and width change is also noticeable. The chromatograms obtained for CO_2 are characterized by lower and wider peaks compared to the peaks obtained under analogous (U = 45 cm/s) conditions for helium (Figure 1). Table 2 presents the averaged peak height ratios of the compounds analyzed for helium (as a carrier and makeup gas—experiment A) to the peak heights obtained for carbon dioxide (experiment B)—detailed data in Table S3a–d.

Table 2. A comparison of carbon dioxide and helium averaged data of GC peak heights and peak widths (at half height) for the test mixture compounds as shown in Figure 1. dh(A/B): peak height (He)/peak height (CO_2); dw (B/A): peak width (CO_2)/peak width (He).

Analytes	dh(A/B)	RSD(h) He [1]	RSD(h) CO_2 [2]	dw(B/A)	RSD(w) He [3]	RSD(w) CO_2 [4]
OCPs	1.84	2.6	1.6	1.73	2.6	2.0
OPPs	1.53	2.2	3.0	1.58	2.2	2.5
PCBs	1.95	1.1	1.3	1.72	2.2	2.0
PAHs	1.76	2.4	3.4	1.58	1.8	2.3
average	**1.77**	**2.1**	**2.3**	**1.65**	**2.2**	**2.2**

[1] RSD(h)He: averaged relative standard deviation of peak high in experiment A, [2] RSD(h)CO_2: averaged relative standard deviation of peak high in experiment B, [3] RSD(w)He: averaged relative standard deviation of peak width in experiment A, [4] RSD(w)CO_2: averaged relative standard deviation of peak width in experiment B.

Considering the average peak height of all compounds for carbon dioxide as a carrier gas (and makeup), it was found to be about 1.8 times lower than for helium. Because the baseline noise for helium and CO_2 were comparable (contaminants effectively retained in gas filters), the sensitivity with helium was about 1.8 times higher than with CO_2 on average (statistically significant differences).

Carbon dioxide provided about 1.6 times wider peaks (at half height) than helium. The peak widths differ slightly for each group of compounds, with a small standard deviation of the compared results (Table 2). When changing the carrier gas from helium to carbon dioxide, the increase in peak width was found to be statistically significant. Thus, the resolution and sensitivity of analyses conducted using CO_2 are lower for the tested flow conditions (similarly as in the case of nitrogen [23,24,26]), which, however, does not significantly affect the separation of most of the analyzed compounds. In the case of this comparison (experiments A and B), the phenomena described are the resultant of effects related to the carrier and makeup gas used.

In additional experiments, analyses of the OCP standard mixture (experiments A and B) were performed using a chromatographic column (column 2) with an analogous stationary phase (like column 1), which had been used to perform many analyses of real samples (which reduced its separation efficiency). For example, the number of theoretical plates (N) for Aldrin was slightly above 24,000 in the case of CO_2 used as a carrier gas (compound no. 6, Figure S3). In the case of the (brand new) column 1 in the experiments described (A to H, Table 1), N was 36,600. As a result of this experiment, it was found that the analysis of the OCP mixture using a column with lower efficiency allows for obtaining a sufficient separation of compounds in most cases (chromatogram: Figure S3). The exceptions are the compounds 12 and 13 (4,4′-DDD, Endrin aldehyde) mentioned earlier, for which Rs was 0.74, and compounds 9 and 10 (4,4′-DDE, Dieldrin): Rs = 1.31. The averaged peak heights and widths (at half height) for all analytes from the OCP group were also estimated. They were dh(A/B) = 2.63 and dw(B/A) = 1.77, respectively. Thus, due to the lower efficiency of column 2, the analyte peaks were more broadened (compared to column 1), which decreased in peak heights. The specified (in Table 2) values of dh(A/B) and dw(B/A) will increase along with the time of using the column for analysis (due to decreasing separation efficiency).

3.3. The Use of CO_2 as a Makeup Gas

As a result of the experiments (C to H), a series of chromatograms were obtained in the conditions of flow or no flow of various makeup gases to the FID detector. Figure 2 shows the chromatograms obtained for Aldrin depending on the carrier gas used and the use (or not) of makeup gas (CO_2 or He).

Comparing the heights of the peaks obtained in experiments D and E with the peaks obtained in experiment C, it was found that they are equal in both cases to about 1.46, i.e., dh(E/C) ≈ dh(D/C). Similarly, when the carrier gas is carbon dioxide (experiments F, G, H): dh(G/F) = 1.32, and dh(H/F) = 1.38 (i.e., dh(G/F) ≈ dh(H/F)).

The results of the remaining compounds belonging to OCPs were similar to those for Aldrin (Table S4). The use of both CO_2 and helium as a makeup gas statistically significantly increases the signal by about 40–50% on average (compared to the situation when no makeup gas was used). This increase is greater (by about 50% on average) when helium is used as a carrier gas, while when CO_2 is used as a carrier gas—the increase is about 40% on average. Due to the fulfillment of the conditions (symbols analogous to those in Table 2): dh(E/C) ≈ dh(D/C), and dh(G/F) ≈ dh(H/F), it can be stated that these changes (Table S4) are independent of the type of gas used as makeup (the differences are not statistically significant). Carbon dioxide can, therefore, be used interchangeably with helium as a makeup gas for FID. At the same time, it is worth mentioning that since dh varies with column efficiency (Section 3.2), the presented peak height changes (i.e., increased sensitivity with makeup gas) depend on specific experimental conditions.

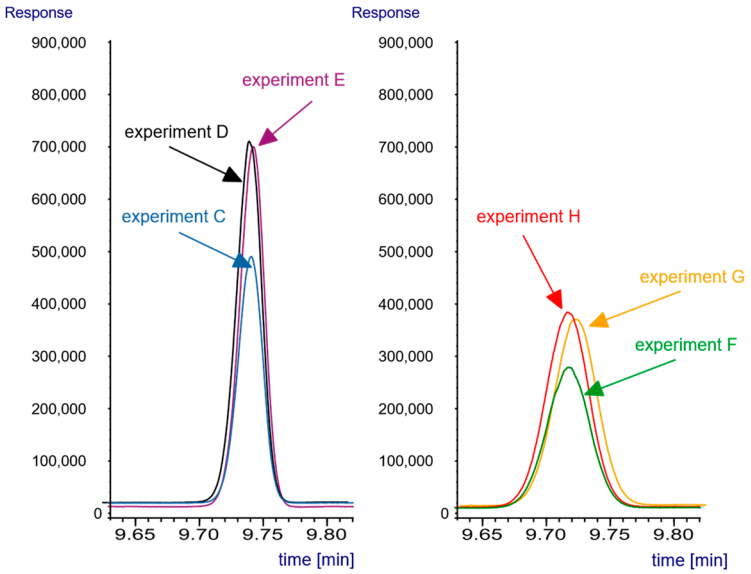


Figure 2. Chromatograms obtained for Aldrin depending on the carrier gas used and the use (or not) of makeup gas (CO_2 or He). Experimental conditions according to Table 1.

4. Conclusions

Carbon dioxide can be successfully used as a carrier gas in capillary gas chromatography (with a non-polar polysiloxane phase) for the analysis of semi-volatile compounds (boiling points of up to 400 °C), after using gas filters that allow for the removal of undesirable components such as oxygen, water, and hydrocarbons. However, the setting of the operating conditions of the chromatograph must be based partly on trial and error because currently, manufacturers do not provide for the use of CO_2 as a gas in GC. As a result of experiments (not yet described in the literature), it was found that for most of the analyzed compounds belonging to the OCPs, OPPs, PCBs, and PAHs, carbon dioxide provides sufficiently high chromatographic resolution even at Q = 2.4 mL/min. Compared with helium used as a carrier gas, carbon dioxide gives broader (about 1.6 times) and lower (about 1.8 times) peaks. For some compounds, the reduction of GC separation efficiency compared to helium is noticeable and leads to incomplete separation (4,4′-DDD, Endrin aldehyde, and two other pairs of compounds with Rs slightly less than 1.5). This effect will be even more visible when the column efficiency is lower (e.g., due to long-term use). It is possible to fully separate all 17 components of the OCP mixture using CO_2 as a carrier gas ($Q \approx 0.4$ mL/min); however, this is associated with an increase in analysis time. Carbon dioxide can also be used as a makeup gas for the FID detector. The signal increase is comparable to that obtained for helium (on average 40–50% depending on the gas used as a carrier). CO_2 can, therefore, be used interchangeably with helium as a makeup gas for FID. To the author's knowledge, such use of carbon dioxide has not been described in the literature so far. When high sensitivity and high resolution are not required, CO_2 can be successfully used as a carrier gas under the same flow conditions as helium. It can, therefore, be implemented for screening analyses, as well as when the composition of the mixture is known and the analytes are not present in low concentrations (e.g., monitoring of model or technological processes) [40,41]. Carbon dioxide can be used in analyses where the sample preparation method is characterized by relatively high selectivity [42,43], as well as in portable devices [32] and when other carrier gases are unavailable. CO_2 can also be utilized as a makeup gas in the FID detector, being an alternative and cheaper gas to helium. However, optimizing its flow and studies considering other groups of compounds should be the subject of further work.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations11120347/s1, Table S1. Literature review on the use of nitrogen and carbon dioxide as carrier gas with WCOT columns; Table S2a. Resolution (Rs) for analytes from the OPP group: Rs(He) for helium as the carrier gas, Rs(CO_2) for carbon dioxide as the carrier gas; Table S2b. Resolution (Rs) for analytes from the PCB group: Rs(He) for helium as the carrier gas, Rs(CO_2) for carbon dioxide as the carrier gas; Table S2c. Resolution (Rs) for analytes from the OCP group: Rs(He) for helium as the carrier gas, Rs(CO_2) for carbon dioxide as the carrier gas; Table S2d. Resolution (Rs) for analytes from the PAH group: Rs(He) for helium as the carrier gas, Rs(CO_2) for carbon dioxide as the carrier gas; Figure S1. Golay curves for α-BHC and Aldrin; Figure S2. Chromatograms of the OCP standard mixture at different volumetric flow rates (Q) when the carrier gas (and makeup gas) is carbon dioxide; Table S3a. A comparison of carbon dioxide and helium averaged data of GC peak heights and peak widths (at half height) for the OPP test mixture compounds as shown in Figure 1. dh(A/B): peak height (He)/peak height (CO_2); dw(B/A): peak width (CO_2)/peak width (He); Table S3b. A comparison of carbon dioxide and helium averaged data of GC peak heights and peak widths (at half height) for the PCB test mixture compounds as shown in Figure 1. dh(A/B): peak height (He)/peak height (CO_2); dw(B/A): peak width (CO_2)/peak width (He); Table S3c. A comparison of carbon dioxide and helium averaged data of GC peak heights and peak widths (at half height) for the OCP test mixture compounds as shown in Figure 1. dh(A/B): peak height (He)/peak height (CO_2); dw(B/A): peak width (CO_2)/peak width (He); Table S3d. A comparison of carbon dioxide and helium averaged data of GC peak heights and peak widths (at half height) for the PAH test mixture compounds as shown in Figure 1. dh(A/B): peak height (He)/peak height (CO_2); dw(B/A): peak width (CO_2)/peak width (He); Figure S3. Chromatogram obtained using column 2 and CO_2 as a carrier and makeup gas for OCPs (1. α-BCH, 2. β-BCH, 3. γ-BHC, 4. δ-BHC, 5. Heptachlor, 6. Aldrin, 7. Heptachlor epoxide, 8. α-endosulfan, 9. 4,4′-DDE, 10. Dieldrin, 11. Endrin, 12. 4,4′-DDD, 13. Endrin aldehyde, 14. 4,4′-DDT, 15. Endosulfan sulfate, 16. Endrin ketone, 17. Methoxychlor); Table S4. Peak height ratios obtained in C-H experiments concerning the effect of makeup gas (m) on the signal using carrier gas: Helium (dh(D/C): peak height (m: CO_2)/peak height (no makeup); dw(E/C): peak height (m: He)/peak height (no makeup)) and carrier gas: CO_2 (dh(G/F): peak height (m: CO_2)/peak height (no makeup); dw(H/F): peak height (m: He)/peak height (no makeup)).

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Conflicts of Interest: The author declares no conflicts of interest.

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