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A New Spectrophotometric Determination of a Pyrethroid Insecticide by Diazotization-Coupling Reaction

Fatimah H. Flayyih*, Abbas N. Alshirifi , Khudheyer J. Kadem

Department of Chemistry, College of Science, University of Babylon, Hilla- 51002, Iraq

***Corresponding author:** fatima841110@gmail.com

Research Article

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Abstract:

A novel and sensitive spectrophotometric technique for identifying alpha-cypermethrin insecticide when coupled with 5-amino-2-hydroxybenzoic acid in an alkaline medium with a pH of about 9–10 was investigated to enhance its analytical detectability to produce yellow-red azo dye. The reaction product was characterized using UV-Vis spectrophotometry (FTIR), ^{1}H-NMR, and ^{13}C-NMR. Acetone and Triton X-100 are used as solvents to increase the solubility and the sensitivity of the procedure. At 25°C, the colored product remained stable for nearly two days. The maximum absorbance was observed at λmax 408 nm. The range of (1-100) µg.mL^{-1} is where the Beer-Lambert law is followed. The developed method was analytically validated. The limit of detection was found to be (0.130) µg.mL^{-1}, and the limit of quantification was (0.433) µg.mL^{-1}, indicating high sensitivity. The process is efficient for large-scale synthesis, has strong functional-group tolerance, and has gentle reaction conditions, suggesting a promising approach for selective and sensitive analytical monitoring in environmental and agricultural samples.

Keywords: Alpha-cypermethrin, Coupling reaction, UV spectroscopy.

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1. Introduction

Alpha-cypermethrin (α-CPM) is known chemically as [Cyano-(3-phenoxyphenyl)-methyl].
3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane-1carboxylate [1].

It is a synthetic pyrethroid insecticide widely used in agriculture, general health, and residential environments to control a broad range of pests. 2. It belongs to the group of chemicals famed as pyrethroids [1,2]. Due to its toxic effects, α-CPM is highly effective against a wide range of insect pests, so it disrupts the normal functioning of the nervous system of insects upon ingestion or contact [3]. α-CPM is used for pest control in various crops such as vegetables, fruits, cereals, and cotton [4], and it protects the yields from damage caused by many insects like caterpillars, beetles, aphids, and mites [5]. In public health programs, it is also employed to combat vectors of diseases such as malaria, Zika virus, and dengue fever by controlling the mosquito numbers [6]. Numerous instrumental methods have been described for the determination of α-CPM, generally analyzed by spectrophotometry [7,8], GC-MS [9], thin layer chromatography (TLC) [10,11], and liquid chromatography-mass [12]. UV spectrophotometry has been used in the evaluation of α-CPM in samples [9].

It's a speed technique that provides rapid analysis with minimal sample preparation; the sensitivity at low concentrations with which it can detect substances depends on the molar absorptivity of the analyte [8,9].

Also, UV-Vis spectrophotometry is versatile, as it can be used for a wide range of compounds, starting from the simple inorganic ions to the complex organic molecules [13,14]. One of the analytical techniques, the UV spectrophotometric method, after coupling reactions in an alkaline medium, is used to determine certain compounds that undergo a specific chemical reaction, resulting in the formation of UV-absorbing or colored products [15]. These methods are extremely useful for quantitative analysis of the compounds that exhibit poor sensitivity or lack inherent UV-V is absorbance in direct measurements [16,17]. Many studies have been conducted on α-CPM. Data on the toxicity and degradation of α-CPM were investigated in India, which aided in understanding the many microbes involved in cypermethrin bioremediation [18]. As it was done, a study on the impact of cypermethrin exposure during pregnancy on maternal and neonatal metabolic status and the biochemical and redox status of α-CPM was investigated [19]. Other research examined the acute and sublethal toxicity caused by α-CPM in the common carp, Cyprinus carpio. Principal component analysis (PCA) and a Pearson correlation matrix were used to analyze the entire biomarker collection [20]. As well, another study separated the enantiomers of α-CPM, and the enantioselective transformation of α-CPM in five soils was investigated [21]. According to a different study, alpha-cypermethrin and spinosad together were a useful tactic for defending stored wheat against a variety of insect pests [22].

In this work, the development of a spectrophotometric method for the determination of α-CPM depends on the diazotized reaction of α-CPM with 5-amino-2-hydroxybenzoic acid (5-AHBA) in alkali media to produce α-CPM-P. Proper optimization of the reaction conditions and the validation of the method are very essential for reliable and accurate results.

2. Experimental

2.1. Material and Methods

(α-CPM) Cyano-(3-phenoxyphenyl)-methyl] 3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane-carboxylate (Alphasin 10% EC-Sineria), 5-AHBA (MERCK), hydrochloric acid 35-38% (SDFCL), acetone 99.8% (SIGMA-ALDRICH), sodium hydroxide 98% (LOBAChemie), sodium nitrite 98% (CDH), sulfamic acid [H_3NSO_3] 99% (Eisen-Golden Laboratories), and Triton X-100 (LAB ALLEY), which were used in this study without further purification.

The products were described using spectroscopic data (FT-IR, UV, H-NMR, and C-NMR) and comparison with primary samples. The IR spectrum was recorded on a Shimadzu FTIR-8400S. UV-visible spectra were recorded on a Shimadzu UV-1800 Double Beam UV/Visible Spectrophotometer. The pH was measured with a pH meter 720 model WTW (Germany). Sensitive digital balance (BP 3015) and Sartorius (Germany) were used.

2.2. General procedure

The coupling reaction between α-CPM and 5-AHBA was conducted under controlled conditions to ensure reproducibility and efficiency. Step 1: A volume of 5 mL of 5-AHBA solution (10^{-3} mol.L^{-1}), prepared by dissolving 0.0153 g of 5-AHBA in 2 mL concentrated HCl, adding 2 mL acetone, and diluting to 100 mL with 0.01% Triton X-100, was mixed with 1.25 mL of 1 mol.L^{-1} HCl and 1 mL of 0.5 mol.L^{-1} $NaNO_2$ solution. This mixture was maintained in an ice bath at 0–5 °C for 10 minutes to facilitate the reaction. Subsequently, 0.25 mL of 0.2 mol.L^{-1} sulfamic acid was added to remove excess sodium nitrite, and the solution was left for an additional two minutes [23]. Step 2: Separately, 5 mL of α-CPM solution (10^{-3} mol.L^{-1}), prepared by dissolving 0.04 g of α-CPM in 100 mL of 0.01% Triton X-100, was adjusted to a final pH of approximately 9.5–10.0 by adding 1 mL of 1.00 mol.L^{-1} NaOH. This pH range was optimized by preparing several solutions with varying pH values and selecting the range that yielded the highest absorbance. The solution from Step 2 was then combined with the mixture from Step 1, stirred briefly, and the total volume was adjusted to 25 mL. The reaction was carried out at low temperature (0–5 °C) and under moderately to strongly alkaline conditions (pH 9–10), without the need for complex instruments or expensive reagents, making the method practical and cost-effective. The resulting complex exhibited a characteristic color, which was quantified by measuring absorbance at λ_{max} 408 nm using UV-Vis spectrophotometry technique.

3. Results and Discussion

3.1. Description of the Product

The resulting precipitate was gathered as a pure, solid-colored material. Using spectroscopic methods such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, and UV-Vis spectroscopy, the structure of the synthesized azo molecule was verified. α-CPM -P absorbance was analyzed in the visible region, with a maximum absorption of wavelength (λ_{max}) at 408 nm, which was used for α-CPM determination (Fig.1).

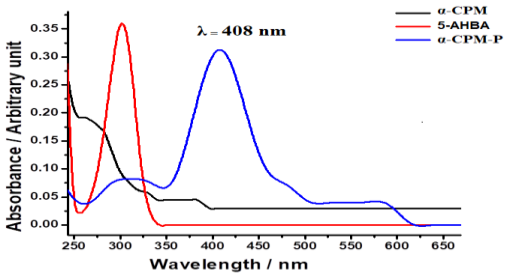


Figure 1. Absorption spectra of α-CPM, 5-AHBA and α-CPM-P at λ_{max} 408 nm.

The existence of important functional groups was

confirmed by distinctive peaks in the FT-IR spectrum, including OH phenol (3227cm^{-1}), C-H aromatic ring (3039cm^{-1}), C-H aliphatic (2924-2865cm^{-1}), CN tripl bond (2163cm^{-1}), C=O ester (1730cm^{-1}), C=N (1680 cm^{1}), and C=C aromatic (1583,1448 cm^{-1}) (Fig. 2). The findings from the proton NMR analysis in DMSO-d6 (400 MHz) corresponded to a singlet at δ 8.99 ppm is attributed to an exchangeable proton (NH), while multiple signals in the aromatic region (δ 7.78–6.5 ppm) correspond to aromatic protons from both the pesticide and the coupling reagent. The aliphatic region displayed signals at δ 3.4 ppm (BrC=CH), δ 2.51 ppm (quartet, CH_2 of ethyl group), and δ 1.18 ppm (triplet, CH_3 group), consistent with the presence of methylene units in the structure. Overall, the spectrum confirms the successful coupling and presence of both aromatic and aliphatic functionalities (Fig. 3). The DMSO-d6 (100 MHz) spectrum (CNMR) exhibited chemical shifts (ppm): 13-40 (CH3, CH alkyl), 60-80 (C-O), 120-130 (C.N. trpil bond). 166-180 (COO. carboxylic and ester (Fig. 4).

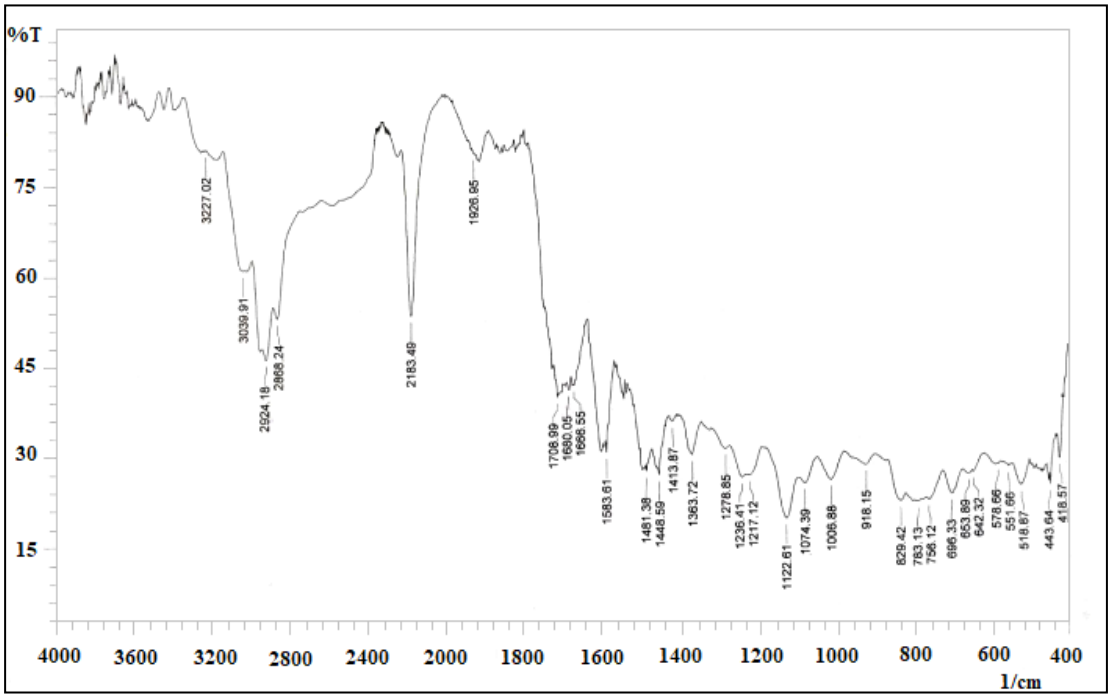


Figure 2. FT-IR Spectrum of the new compound (α-CPM-P).

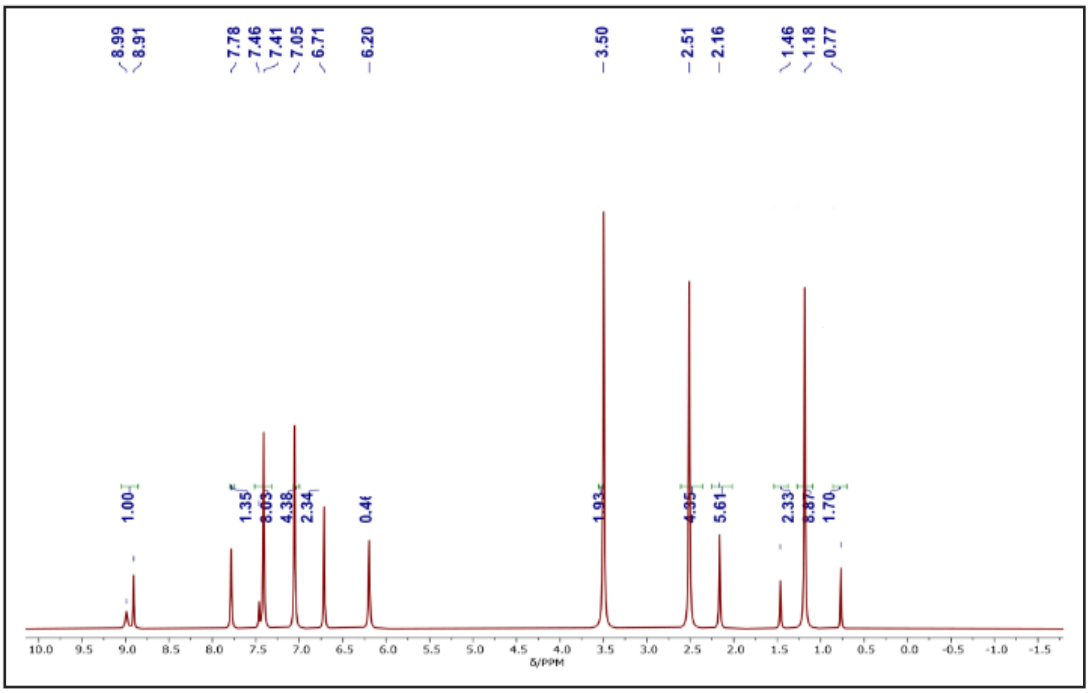


Figure 3. ^{1}H-NMR Spectrum of the new compound (α-CPM-P).

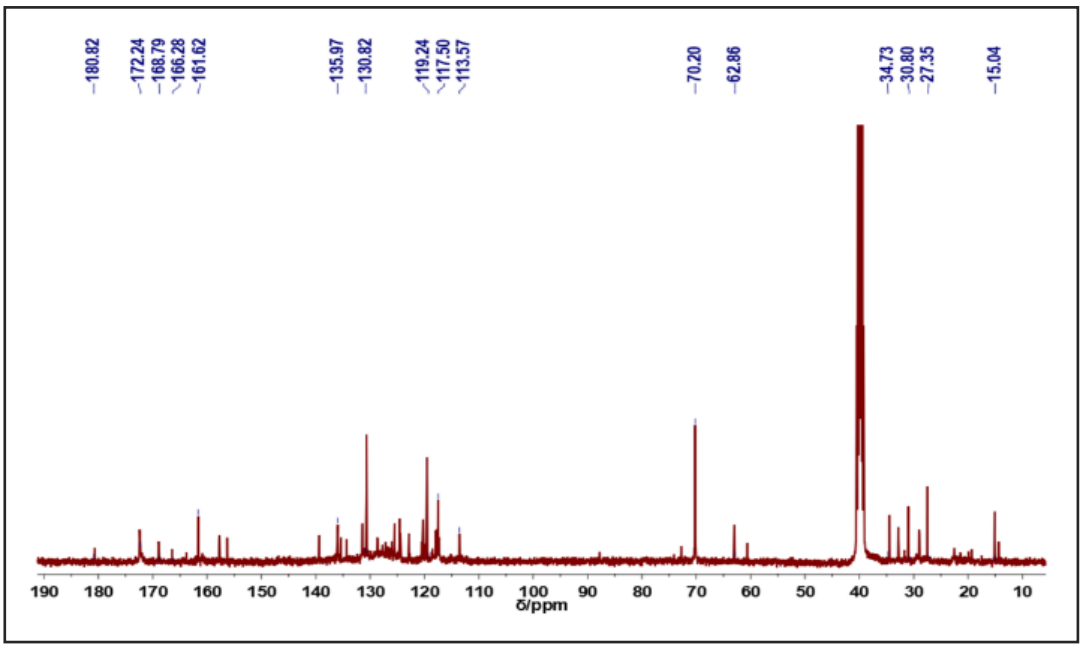
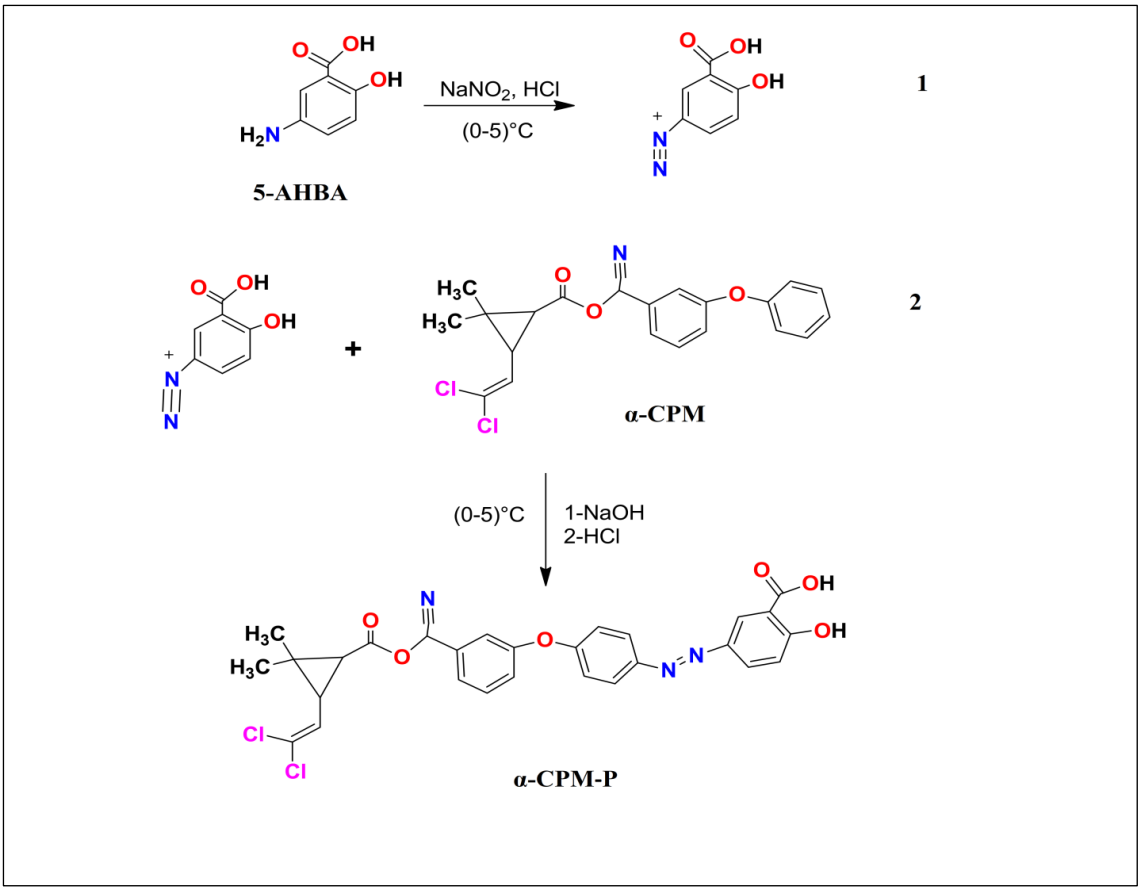


Figure 4. ^{13}C-NMR Spectrum of the new compound(α-CPM-P).

3.2. Reaction of α-CPM with 5-AHBA

The azo compound is created by a diazotization-coupling reaction. In order to create the diazonium salt, 5-AHBA first undergoes diazotization at low temperatures (0–5°C) with sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl). The azo bond (–N=N–) and the final colorful product are formed when this highly reactive intermediate and α-CPM engage in an electrophilic coupling process. The reaction follows a classical electrophilic substitution mechanism, where the diazonium ion acts as an electrophile, attacking the activated aromatic system of α-CPM. Scheme 1 shows both the expected initial reaction as well as the formation of the azo compound.



Scheme 1. The suggested reaction between α-CPM insecticide with 5-AHBA.

3.3. Optimization of reaction conditions

Numerous experimental parameters that affected the azo compound's synthesis were methodically improved. The best conditions for the diazotization and coupling reactions were determined by examining the effects of reagent volumes, reaction duration, and temperature on absorbance.

3.3.1. *Effect of volumes*

Different volumes of 5-AHBA (0.5–4.0) mL at concentration 10^{-3} mol.L^{-1} are used in the spectrophotometric determination of α-CPM, and the results show that the best absorbance was obtained at volume 2 mL. The impact of the volume of NaOH was examined, different volumes of 1.00 mol.L^{-1} NaOH solution (0.25-1.50) mL are used in the spectrophotometric determination of α-CPM, as in the mentioned procedure. The results indicate that the best absorbance was at volume 1.0 mL. The effect of HCl volume was studied by using different volumes of the 1.00 mol.L^{-1} HCl solution (0.25-2.00) mL used in the spectrophotometric determination of α-CPM. The results show that the best absorbance was obtained at volume 1.25 mL. The acid medium is necessary to protonate the amine group, making it more reactive towards nitrous acid [24]. The effect of Sodium Nitrite volume was studied with different volumes of the 0.50 mol.L^{-1} $NaNO_2$ solution (0.25-2.50) mL used in the determination of α-CPM, and the results show that the best absorbance was obtained at volume 1.50 mL. $NaNO_2$ is essential for the diazotization reaction, facilitating the conversion of primary aromatic amines to diazonium salts [25]. The optimum volumes of 5-amino-2-hydroxybenzoic acid, NaOH, HCl, and $NaNO_2$ are explain in (Fig. 5 A).

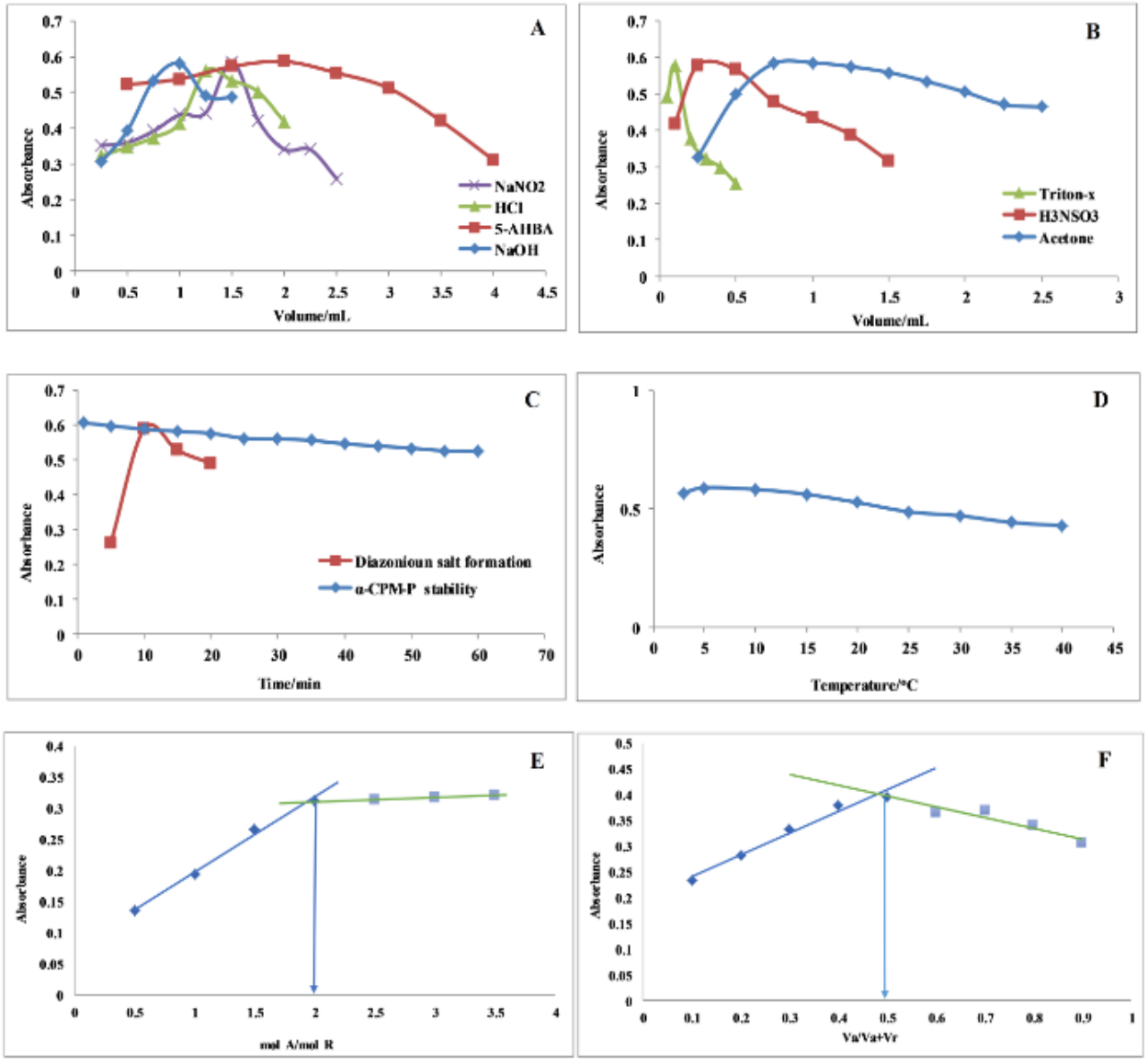


Figure 5. The volume effect of (**A**) NaOH, HCl, $NaNO_2$ and 5-AHBA (**B**) H_3NSO_3, Triton X and Acetone, (**C**) The effect of time in minutes on the compound formation and the compound stability, (**D**) Temperature Effect on the compound formation (**E**) Molar ratio for α-CPM reaction with 5-AHBA, and (**F**) Jobs method for α-CPM reaction with 5-AHBA

Also by using various acetone volumes, the impact of acetone volume was investigated. (0.25-2.50) mL at different percentages (0.50-5.00), respectively, are used in the spectrophotometric determination of α-CPM. The results show that the absorbance was equal at volumes (0.75-1.00) mL (1.5-2%), which gives the best result. Acetone is a polar aprotic solvent, meaning it can dissolve a wide range of polar and nonpolar substances, and when added to the solution, it increased the solubility of α-CPM particles that contribute to turbidity, thus improving clarity [26]. The effect of sulfamic acid volume was examined at different volumes of 1.00 mol.L^{-1} of sulfamic acid (0.10–1.50 mL) is used in the spectrophotometric determination of α-CPM. Sulfamic acid plays a crucial role in diazo coupling reactions by providing the necessary acidic environment for diazonium salt formation and serving as a coupling agent for the synthesis of azo compounds [23, 27]. The results show that the best absorbance was 0.25 mL. The effect of Triton X-100 volume was examined, different volumes of 0.01 % Triton X-100 (0.05-0.5) mL are used in the spectrophotometric determination of α-CPM, and the results show that the best absorbance was (0.1) mL. Triton X-100 acts as a surfactant often utilized in emulsification, solubilization of hydrophobic compounds, and increasing the stability of colloidal suspensions [28]. All the volumes of acetone, sulfamic acid, and Triton X-100 were explains in (Fig. 5 B).

3.3.2. *The effect of Time and Temperature*

It was investigated how time affected the compound stability.

The compound exhibited good stability over time, as demonstrated by the effect of the absorbance used to determine α-CPM on the stability time. Also, the required time effect for the diazonium salt formation was examined; the impact of the desired amount of time to finish diazonium salt formation on the absorbance employed for the spectrophotometric determination of α-CPM revealed that the formation of diazonium salt takes 10 minutes to complete, as shown in Fig. 5C. Also, the impact of varying temperatures on absorbance was examined in order to determine α-CPM spectrophotometrically, as appears in Fig. 5D.

3.3.3. *Determination of reaction stoichiometry*

By molar ratio method, it's used to analyze the results obtained from the reaction between α-CPM and 5-AHBA in order to determine the stoichiometry of the reaction as show in (Fig. 5 E). And by Job's method, the (1*10 $^{-4}$ mol.L^{-1}) concentration used for both of α-CPM and 5-AHBA, this experiment important to provide insights into the stoichiometry of complex formation reactions, helping to elucidate the composition of complex ions. As shown in the (Fig. 5 F).

3.3.4. *Analytical parameters and the suggested method's validity*

Under ideal circumstances, we made a range of α-CPM solutions with concentrations between 1 and 100 µg/mL, including 5-AHBA. As seen in Fig. 6, a calibration curve was created by charting absorbance against concentration after the absorbance of the newly synthesized chemical was recorded at 408 nm. The intercept was used to calculate the limit of detection (LOD) and the limit of quantification (LOQ).

Also the analytical parameters of the suggested approach are compiled in Table 1.

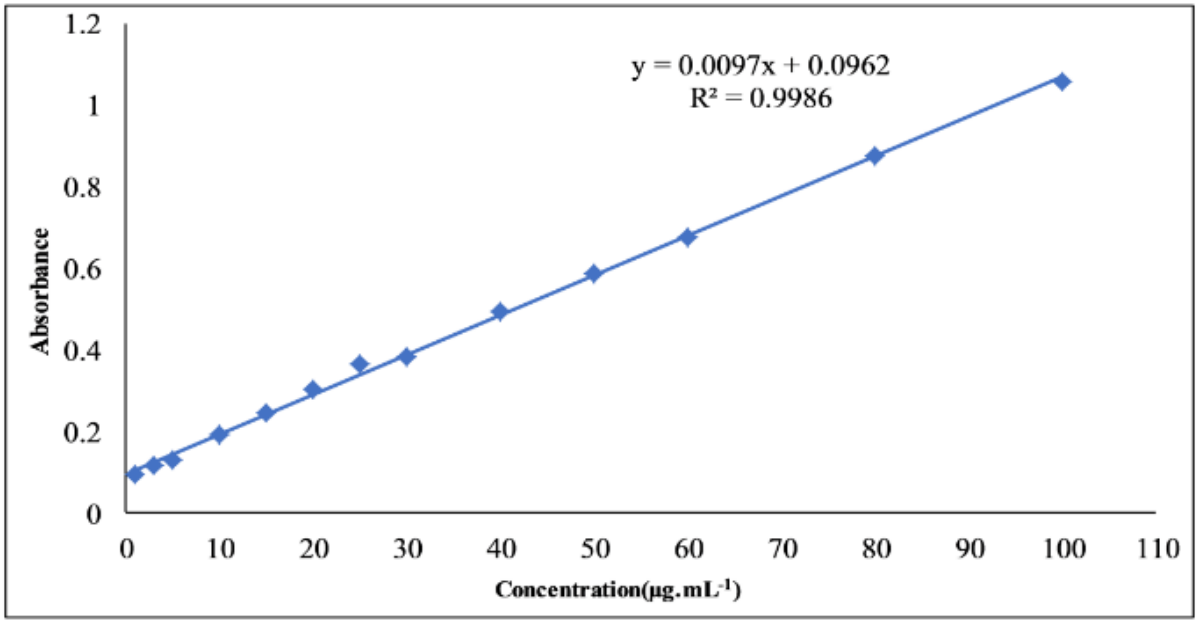


Figure 6. Calibration curve for the diazotization new compound (α-CPM-P).

3.3.5. *Accuracy and Precision*

The purpose of repeatability studies was to evaluate work accuracy. The test was carried out by choosing three concentrations (30, 40, and 50) $\mu g.mL^{-1}$ of the sample solution from the calibration curve and repeating the experiment four times for each concentration. The percent recovery (Rec %) indicates that the proposed method is highly accurate. Also, to ensure the suggested procedure precision, three concentrations of α-CPM (40, 60, and 80) $\mu g.mL^{-1}$were prepared and analyzed. The results' R.S.D.% was less than 2, indicating an accuracy level that is appropriate. Table 2 displays the accuracy and precision results.

Table 1. The analytical parameters of the proposed method.

Parameter	value
λexc, nm	385
λem, nm	605
Linear range (µg.mL-1)	1-100
Slope	0.0097
Determination coefficient r2	0.9986
Correlation coefficient r	0.9979
Intercept	0.0962
Limit of detection (µg.mL-1)	0.130
Limit of quantification (µg.mL-1)	0.433

Table 2. Accuracy and Precision details

Accuracy details of the suggested method				
Sample	Taken Conc. ($\mu g.mL^{-1}$)	Found Conc. ($\mu g.mL^{-1}$)	E % ± SD	Rec %*
1	30	29.695	-1.013± 0.009251	98.98 %
2	40	40.623	1.559± 0.018025	101.55 %
3	50	50.675	1.350± 0.014431	101.35 %

Precision details for the suggested method					
Sample	Conc. ($\mu g.mL^{-1}$)	Intra-day precision		Inter-day precision	
		RSD%	Rec%	RSD%	Rec%
1	40	99.82	1.458	100.06	1.394
2	60	99.27	1.035	99.92	0.974
3	80	100.94	1.044	100.72	0.839

**Mean of four determinations*

3.3.6. *Effect of α-CPM on soil*

The proposed method was applied for the determination of α-CPM after the treatment in various concentrations (40, 50, 60) $\mu g.mL^{-1}$. Results show that the weight-volume ratio of α-CPM for all concentrations was calculated; about more than half of the insecticide will leach into the soil, as shown in Table 3. Also, a statistical comparison has been made between the outcomes of the recommended approach and those obtained. Table 4 provides a statistical explanation of several key techniques utilized in the determination of α-CPM and the recommended procedure that were satisfactory in recovery value. The technique can identify minute concentrations of the pesticide.

Table 3. Results of α-CPM on soil of the suggested method

Sample	Taken Conc. ($\mu g.mL^{-1}$)	Found Conc. ($\mu g.mL^{-1}$)	Rec %* after application on soil
1	40	27.814	69.536
2	50	30.082	60.164
3	60	28.845	48.075

**Mean of four determinations*

4. Conclusions

Aryl diazonium products are easily prepared from amine compounds. The formation of a diazonium salt could indicate the presence of certain functional groups or moieties in the α-CPM molecule, so this information can be crucial for identifying and characterizing the chemical structure of the insecticide. The leaving group (N2) does not interfere with the mixture of reactions. Also the coupling reaction proceeds with high chemo selectivity and sensitivity for α-CPM, which is valuable for environmental monitoring or quality control purposes. One of the important sides is the toxicological implications: it may alter the toxicity profile of α-CPM, diazonium salts can be highly reactive and potentially more toxic than the parent compound, it may be more effective for the insect's combat. The suggested method is simple, rapid, sensitive, and inexpensive for the determination of α-CPM.

5. Acknowledgement

I want to express my gratitude to the Ministry of Agriculture for giving me the opportunity to complete my pesticide studies and research.

Table 4. Comparative analysis of methods for determining α-CPM

Technique	Linear range		RSD %	Rec %	LOD		LOQ		Ref.
GC-MS	0.10-12	$mg.L^{-1}$	2.1-5.0	83.90-93.15	0.03	$mg.L^{-1}$	------	------	[9]
GC-MS	1-500	$\mu g.mL^{-1}$	------	82.1-92.7	0.17	$\mu g.mL^{-1}$	------	------	[29]
GC-MS	1-400	$\mu g.mL^{-1}$	------	-------	0.5	$\mu g.mL^{-1}$	1	$\mu g.mL^{-1}$	[30]
LC-MSMS, GC-MS	------	------	15.05	98.12	4.43	$\mu g.mL^{-1}$	15	$\mu g.mL^{-1}$	[31]
GC-μECD	0.05-10	$g.kg^{-1}$	3.5	86-107	0.0094	$g.kg^{-1}$	0.031	$g.kg^{-1}$	[32]
FT-IR	0.64-1.87	$mg.g^{-1}$	0.4	------	0.7	$mg.g^{-1}$	2.3	$mg.g^{-1}$	[33]
UV	1-100	$\mu g.mL^{-1}$	0.51	98.98-101.55	0.13	$\mu g.mL^{-1}$	0.433	$\mu g.mL^{-1}$	current study

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