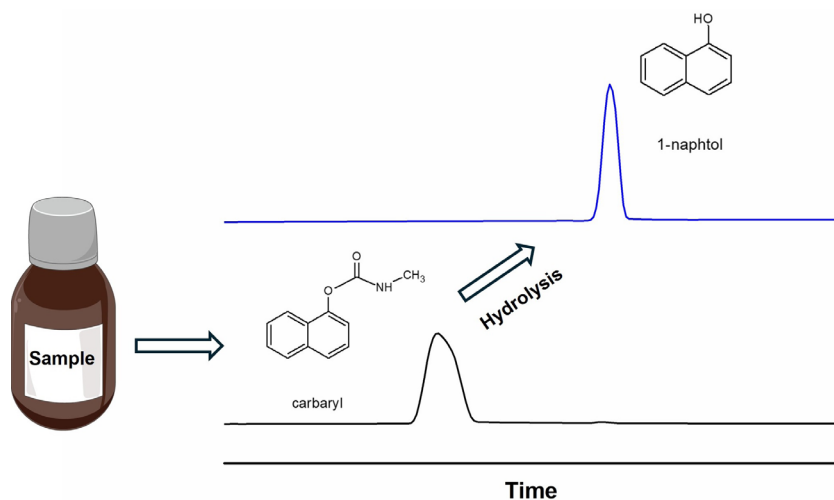


ARTICLE

Simple and Fast Determination of Carbaryl Pesticide in Commercial Topical Formulations by Capillary Electrophoresis

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A novel analytical method using capillary zone electrophoresis (CZE) for simple and fast determination of the pesticide carbaryl in commercial topical formulations was developed and validated. The carbaryl was previously hydrolyzed quantitatively under an alkaline medium (NaOH solution) to form 1-naphthol, which was separated and quantified by CZE with spectrophotometric detection at 214 nm. Optimization of the hydrolysis reaction regarding time and NaOH concentration was conducted. The CZE separation was achieved in less

than 3 min using a bare silica capillary (60 cm total length) and a 10 mmol L⁻¹ sodium borate buffer (pH 9.3) as background electrolyte. The proposed CZE method was linear in the 0.25 to 70 mg L⁻¹ concentration range, as attested by a coefficient of determination (R²) higher than 0.999 and confirmed by the lack of fit test. Recovery tests at three concentration levels provided recovery percentages ranging from 80 to 115%, indicating acceptable accuracy. The limits of detection (LOD) and quantification (LOQ) were 0.08 and 0.25 mg L⁻¹, respectively. The proposed CZE method was successfully applied for carbaryl determination in commercial samples of topical formulations such as powders and dry bath gel.

Keywords: carbaryl hydrolysis, indirect quantification, 1-naphthol, pesticides, quality control

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INTRODUCTION

Carbaryl (1-naphthyl-N-methyl carbamate) is a pesticide belonging to the carbamate family that is widely used in several countries to control more than 100 species of insects, particularly in feed crops.^{1,2} Carbaryl has also been an active compound in commercial formulations against parasites (fleas, ticks, mites, and lice) in dogs, cats, and livestock. Carbaryl kills the insects by acting on the inhibition of the enzyme acetylcholinesterase (AChE), with consequent accumulation of the neurotransmitter acetylcholine in the organism.^{1,2}

Carbaryl is considered a safer pesticide than others, such as the organophosphorus class, because of its lower toxicity and faster biodegradation. However, the extensive use and occupational exposition of this pesticide have been causing concerns worldwide because of its neurotoxicity and low degradation at anaerobic conditions (i.e., half-life of 72 days in soils).³ For monitoring carbaryl concentrations in different samples, developing analytical methods is essential for toxicology studies, food safety, environmental monitoring, and quality control of commercial products containing carbaryl as the active ingredient.⁴⁻⁶ Carbaryl has mostly been determined by analytical methods using high-performance liquid chromatography (HPLC),⁷⁻⁹ spectrophotometry,¹⁰⁻¹⁶ fluorescence,¹⁷ electrochemical techniques,^{13,18} and biosensors.¹⁹

Capillary electrophoresis (CE) can be an interesting analytical technique for carbaryl determination.²⁰⁻²⁵ CE has the advantages of being fast, requiring a small amount sample, and producing low volumes of residue. Thus, CE has been considered a green analytical technique for determining several pesticides.^{26,27} Capillary zone electrophoresis (CZE) is the simplest and widest-used CE separation mode. However, carbaryl is not ionizable, preventing it from being directly determined by CZE. To overcome this limitation, usually, alkaline hydrolysis of the carbaryl (Figure 1) is conducted to obtain 1-naphthol, which can be quantified by CZE.²⁰⁻²²

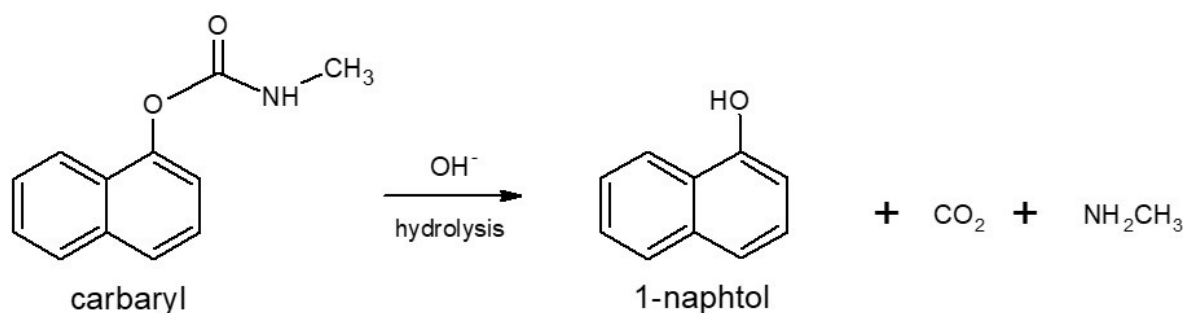


Figure 1. Alkaline hydrolysis reaction of carbaryl.

The determination of carbaryl in commercial formulations is essential for the pest control industry and regulatory agencies to ensure the quality control and safety of these products. Despite the simplicity, quickness, reliability, and environmental-friendliness of the CZE, this separation technique has never been reported to quantify carbaryl in such formulations.

In this work, for the first time, CZE was used to indirectly determine the carbaryl pesticide after simple alkaline hydrolysis in commercial topical formulations (powders and dry bath gel). The proposed method was validated and demonstrated to be suitable for applications in quality control and safe assessment of such products.

MATERIALS AND METHODS

Reagents and solutions

All reagents were of analytical grade. Carbaryl and 1-naphthol were obtained from Sigma-Aldrich (Steinheim, Germany). Ethanol, HCl, NaOH, and Na₂B₄O₇·10H₂O (borax) were purchased from Labsynth (Diadema, SP, Brazil). A purification system (Millipore, Molsheim, France) produced ultrapure water.

A stock solution of carbaryl at a concentration of 500 mg L⁻¹ was prepared by dissolving the proper amount of the reagent in methanol and kept in a refrigerator (4° C). An aqueous standard stock solution of 1-naphthol (2.5 mmol L⁻¹) was prepared and diluted as required with ultrapure water to obtain the work standard solutions used to acquire the calibration curves. The background electrolyte (BGE) was prepared daily by dissolving a mass of 0.0477 g of borax in 50 mL of ultrapure water. The resulting BGE was a 10 mmol L⁻¹ borate buffer solution used without further pH adjustment that was 9.3.

CZE procedure

CZE separations were conducted in a CE system, Agilent 7100 CE (Agilent Technologies, Waldbronn, Germany), equipped with a diode array detector (DAD) and a bare fused silica capillary with a total length of 60 cm (52 cm effective) and 50 µm of internal diameter. Before the first run of the day, the capillary was conditioned by flushes with methanol (10 min), HCl 1 mol L⁻¹ (10 min), water (5 min), NaOH 0.1 mol L⁻¹ (10 min), water (5 min), and BGE (10 min). The separation voltage was 25 kV, the temperature was 25 °C, spectrophotometric detection was at 214 nm, and the samples were hydrodynamically injected (5 s at 50 mbar) into the CE system. A short flush (1 min) with BGE was performed between the separation runs to ensure the capillary was cleaned from remained compounds from the previous sample injection. The BGE in the reservoirs was renewed after every 10 runs to reduce the pH changes caused by the electrolysis. After its use, the capillary was stored empty after being cleaned (flushed) with HCl 1 mol L⁻¹ (10 min), water for (5 min), and air (10 min).

Optimization of the carbaryl hydrolysis

The concentration of the NaOH and the reaction time were optimized to achieve quantitative hydrolysis of the carbaryl. Thus, NaOH concentrations of 1, 2, 4, 6, 8, and 10 mmol L⁻¹ were evaluated for hydrolysis of standard solutions containing 40 mg L⁻¹ of carbaryl. Additionally, the hydrolysis times of 0, 5, and 10 min after adding NaOH and homogenization steps were assessed.

Sample preparation

Four samples of commercial topical formulations containing carbaryl (three in powder form and one as a dry bath gel) were purchased from the local market in the city of Campinas, SP, Brazil. These products are usually applied in pets to combat external parasites (fleas, mites, ticks, and lice). A mass of 0.05 g of the powder samples was weighed into a beaker, and 4 mL of ethanol was added to extract the carbaryl with the aid of a sonication bath for 15 min. The suspension was transferred to a 25 mL volumetric flask and 50 µL of NaOH (1 mol L⁻¹) solution was added to give a final concentration of 2 mmol L⁻¹ after the flask was filled with ultrapure water. A similar sample preparation was conducted for the dry bath gel, but a higher sample mass (2 g) was required, and ethanol was unnecessary.

All prepared samples were filtered through a poly(vinylidene fluoride) (PVDF) membrane filter (0.22 µm) to prevent particles in the solution samples injected into the CE system.

Analytical parameters assessment

A calibration curve was obtained for the linearity evaluation using work standard solutions of 1-naphthol prepared (in triplicate, each) with a concentration range corresponding to 0.25 to 70 mg L⁻¹ of carbaryl. The determination coefficient (R²) from the linear regression and a lack of fit test²⁸ were used to assess the linearity of the proposed method. The limits of detection (LOD) and quantification (LOQ) were determined by calculating the concentrations that yielded peak heights three times and ten times greater than the signal-to-noise ratio of the baseline in the electropherograms, respectively. Intraday precision was evaluated by obtaining the relative standard deviation (RSD) of three independent determinations of carbaryl conducted on the same day. Interday precision was determined by calculating the RSD of carbaryl quantifications taken across three separate days. The recovery tests were conducted at three concentration levels of carbaryl. For these tests, after the weighting step, the samples were spiked with a suitable volume of

the standard stock solution of carbaryl to achieve the desired concentration level. After the spiking, the samples underwent the same sample preparation described earlier. The recovery percentages were calculated according to Equation 1.

$$\text{Recovery (\%)} = \frac{C_f - C_0}{C_{\text{add}}} \times 100 \quad \text{Equation 1}$$

where C_f was the concentration found in the sample after spiking with carbaryl, C_0 was the concentration of carbaryl in the sample before the spiking, and C_{add} was the final concentration of carbaryl added to achieve the spiking concentration level.

RESULTS AND DISCUSSION

Optimization of CZE separation

Figure 2 shows electropherograms of standard solutions of 1-naphthol (200 $\mu\text{mol L}^{-1}$) and carbaryl (40 mg L^{-1}) without and after the alkaline hydrolysis reaction. Although carbaryl is neutrally charged, its peak could be observed because it was driven to the detector by the electroosmotic flow (EOF). Thus, carbaryl could be directly detected (without hydrolysis), but any other electrically neutral compound could cause peak overlapping (interference). However, after optimized alkaline hydrolysis, the carbaryl was quantitatively converted to 1-naphthol (Figure 1), which was quantified using CZE-DAD to determine the carbaryl indirectly. The 1-naphthol separation was performed in the counter-EOF mode in less than 3 min with a good peak shape (Figure 2). This CZE separation mode is advantageous for anionic compounds with low electrophoretic mobility, such as 1-naphthol, because no EOF reversion is required, simplifying the composition of the BGE. Borate buffer solution (10 mmol L^{-1}) was chosen as BGE because its high natural pH (9.3) provides a high EOF. Additionally, this BGE has low UV absorption, making it appropriate for spectrophotometric detection. Using this BGE, the wavelengths of 210, 214, 230, and 254 nm were evaluated for the spectrophotometric detection of 1-naphthol. The highest peak area (data not shown) was achieved using 214 nm, which was chosen for further studies.

Optimization of carbaryl hydrolysis

The efficiency of the alkaline hydrolysis reaction was optimized using a 40 mg L^{-1} carbaryl solution that underwent hydrolysis using NaOH at the concentrations of 1, 2, 4, 8, and 10 mmol L^{-1} . The peak areas of the produced 1-naphthol were compared with that obtained for a standard solution of 1-naphthol (200 $\mu\text{mol L}^{-1}$) with concentration expected for a quantitative hydrolysis of the 40 mg L^{-1} carbaryl solution. Among the NaOH concentrations evaluated, only the 1 mmol L^{-1} could not provide quantitative hydrolysis of the carbaryl solution, even with 10 min waiting after the NaOH addition, as depicted in Figure S1 (Supplementary Material). Thus, a concentration of NaOH at 2 mmol L^{-1} was chosen to avoid injecting strong alkaline solutions into the CE system. Regarding the hydrolysis time, complete hydrolyses of carbaryl were achieved for 0, 5, and 10 min after adding NaOH with final concentrations equal to or higher than 2 mmol L^{-1} . Figure 2 shows an electropherogram obtained using the optimized hydrolysis conditions using a NaOH concentration of 2 mmol L^{-1} without waiting time.

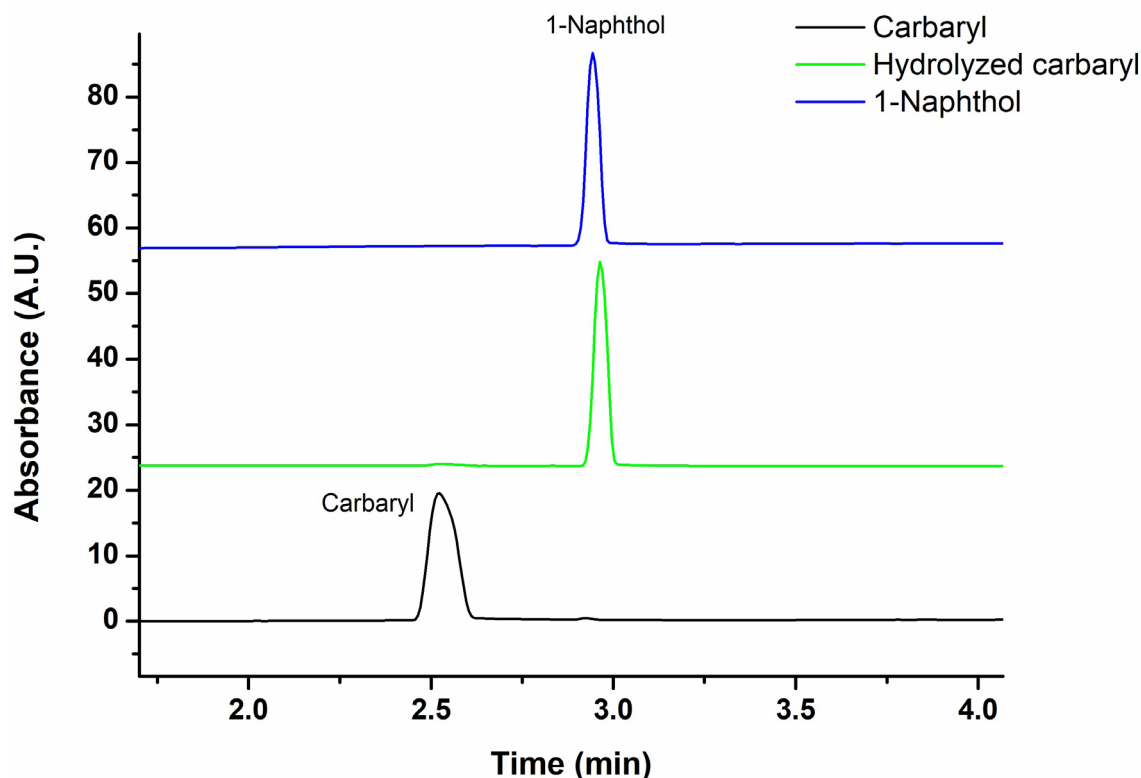


Figure 2. Electropherograms of standard solutions of carbaryl (40 mg L^{-1}) without hydrolysis, 1-naphthol ($200 \text{ } \mu\text{mol L}^{-1}$), and carbaryl (40 mg L^{-1}) after alkaline hydrolysis (2 mmol L^{-1} NaOH). Separation conditions: BGE: 10 mmol L^{-1} sodium borate buffer (pH 9.3); bare fused silica capillary with a total length of 60 cm (52 cm, effective) and $50 \text{ } \mu\text{m}$ i.d.; hydrodynamic sample injection for 5 s at 50 mbar; separation voltage of 25 kV; spectrophotometric detection at 214 nm.

Analytical parameters of the proposed method

After the optimization of alkaline hydrolysis, some analytical parameters were assessed, as depicted in Table I. The precision of the migration time for the 1-naphthol was 1% (RSD), demonstrating good run repeatability. The separation efficiency measured by the number of plates per meter is compatible with those usually obtained in CZE. The linearity of the method was attested by the value of the coefficient of determination (R^2) higher than 0.999 and by the lack of fit results, with $F\text{-value} < F_{\text{tab}}$ (2.74) and $P\text{-value} > 0.05$. The LOD and LOQ were considered suitable for the concentration range of carbaryl found in the analyzed samples, as discussed in the following section.

Table I. Analytical parameters of the CZE method for carbaryl determination

Analytical Parameter	
Migration time (min) ^a	2.86 ± 0.03
N/m^b	41,681
Linear calibration range (mg L^{-1}) ^c	0.25-70
Slope	1.879 ± 0.0193
Intercept	0.897 ± 0.923

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Table I. Analytical parameters of the CZE method for carbaryl determination (continuation)

Analytical Parameter	
Coefficient of determination (R^2)	0.9995
Lack of fit ^d	P-value = 0.14
	F-value = 1.64
LOD (mg L^{-1}) ^e	0.08
LOQ (mg L^{-1}) ^e	0.25

^aMean \pm standard deviation for 7 consecutive replicate runs; ^bNumber of plates per meter; ^ccalibration curve obtained in triplicate ($n = 3$); ^d95% significance level; ^eLimits of detection and quantification were calculated for a signal-to-noise ratio of 3 and 10, respectively.

Table II summarizes the results of the recovery tests, showing recovery levels varying from 80 to 115% and a maximum standard deviation of 7%. These results fall within the recovery range of 80-120%, usually accepted for quantitative analysis,²⁹ indicating that the proposed CZE method shows acceptable accuracy.

Table II. Results of the recovery tests at three concentration levels

Sample	Conc. Added (mg g^{-1})	Conc. Found (mg g^{-1})	Recovery (%) ^a
Powder 1	10	11.5	115 \pm 4
	20	22	110 \pm 7
	30	30.9	103 \pm 3
Powder 2	10	9.4	94 \pm 6
	20	17	85 \pm 6
	30	27.3	91 \pm 7
Powder 3	10	9.0	90 \pm 6
	20	19.8	99 \pm 7
	30	24.9	83 \pm 2
Dry bath gel	0.25	0.20	82 \pm 2
	0.50	0.40	80.0 \pm 0.5
	0.75	0.60	80 \pm 1

^a $n = 3$

Application of the CZE method

Figure 3 shows electropherograms from the analysis of the samples of commercial topical formulations.

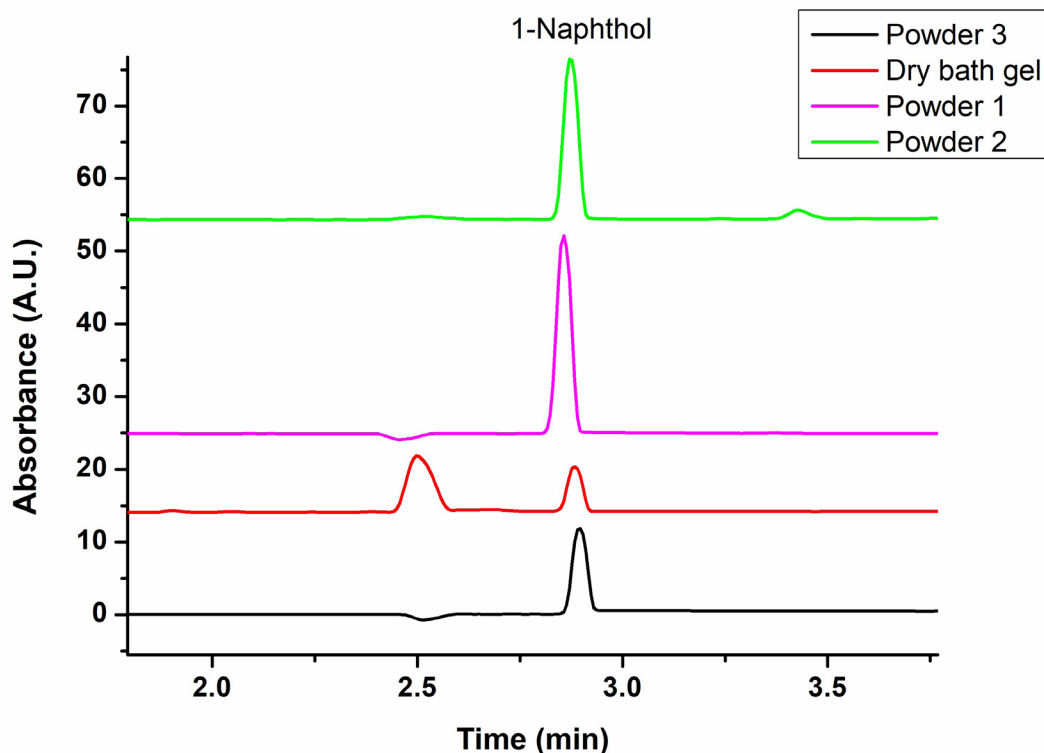


Figure 3. Electropherograms of the analyzed samples of commercial topical formulations containing carbaryl. Separation conditions as in Figure 2.

In addition to the peak attributed to 1-naphthol, the electropherograms (Figure 3) reveal additional peaks corresponding to other compounds (unidentified) present in the composition of the analyzed samples. Moreover, the peak purity (data not shown) of 1-naphthol, as assessed by the DAD of the CE system, demonstrated that the CZE separation effectively minimizes interference from the sample matrix.

Table III shows the concentrations of carbaryl found in the analyzed samples and compares them with those labeled.

Table III. Results of the sample analysis using the proposed method

Sample	Conc. Labeled ^a (mg g ⁻¹)	Conc. Found (mg g ⁻¹) ^b	Error (%)
Powder 1	20	28.8 ± 1.6	44
Powder 2	20	20.5 ± 0.7	2.5
Powder 3	10	9.4 ± 0.3	-6
Dry bath gel	0.15	0.11 ± 0.01	-27

^ainformed by the manufacturer; ^bn = 3

The concentration of carbaryl in the sample Powder 1 was 44% higher than that informed by the manufacturer. On the other hand, a good concordance between the carbaryl concentrations was found for the other powder samples. As the matrices of the powder samples were similar and the proposed CZE method demonstrated good selectivity and acceptable accuracy, the discrepancy of the carbaryl concentration found for the sample Powder 1 may most be attributed to some issues related to the manufacturing process (quality control). Another concentration divergence was found for the dry bath gel,

in which the carbaryl concentration was 27% lower than that labeled. Despite the recovery percentages for this sample being acceptable, a comparison with a reference method could provide additional evidence to confirm this concentration difference.

For the analyzed samples, the intraday precision (RSD) of the concentrations varied from 3.2 to 5.6% ($n=3$), and the interday precision ($n=3$) ranged from 5 to 6%. These RSDs, with the highest values close to 5%, can be considered acceptable for quantitative analysis.²⁹

Comparison with other methods

Table IV compares the proposed method with other methods that reported carbaryl determination in formulations. The linear concentration range of the CZE method (0.25-70 mg L⁻¹) can be considered comparable with the other methods except for that using gas chromatography (GC),³⁰ which has a wider linear range (1-1000 mg L⁻¹). On the other hand, the LOD (0.08 mg L⁻¹) of the proposed method was better than that showed by the GC method and was close to those of the other methods, except for that (0.002 mg L⁻¹) achieved by the method using flow-injection analysis (FIA) with amperometric detection.¹³ The recovery percentages of the CZE method showed a higher variation (80–115%), but it still demonstrated suitable accuracy for the quantitative analysis of carbaryl in the analyzed samples. Additionally, the CZE method can be considered more straightforward and faster than the methods that require a laborious and time-consuming derivatization step following the alkaline hydrolysis.^{13–15}

CONCLUSIONS

We developed and validated a CZE method for reliable indirect determination of carbaryl in commercial topical formulations, making the first application of this separation technique for such analysis. The proposed CZE method demonstrated reliability, simplicity, and quickness for determining carbaryl in the analyzed samples. Because the proposed method indirectly quantifies carbaryl by detecting a hydrolysis product (1-naphthol) of this pesticide, the method accuracy can be affected by 1-naphthol from other sources than carbaryl hydrolysis. Additionally, some sample matrices can potentially interfere with the efficiency of the hydrolysis reaction, requiring further optimizations, particularly in the NaOH concentration. Despite these limitations, we believe this method can be useful for the quality control and safety assurance of commercial formulations containing carbaryl as an active compound. Moreover, the method can be a starting point or adapted for determining carbaryl in other matrices samples beyond topical formulations, extending to new applications, such as environmental monitoring, food safety, and toxicology studies.

Table IV. Comparison between the proposed CZE method with others for the determination of carbaryl in formulations

Technique	Experimental details	Linear range (mg L ⁻¹)	LOD (mg L ⁻¹)	Recovery (%)	Ref.
Capillary zone electrophoresis	Indirect quantification ^a using alkaline hydrolysis	0.25-70	0.08	80-115	This work
Spectrophotometry	Indirect quantification ^a using alkaline hydrolysis and derivatization	2.01-60.3	-	87.6-92.8	14
Gas Chromatography	Direct quantification	1-1000	0.5	98.5-100.8	30
Chemiluminescence, using flow-injection techniques	Reaction with Ce(IV) in acid medium containing rhodamine	0.05-2	0.045	94.5-101.5	31

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Table IV. Comparison between the proposed CZE method with others for the determination of carbaryl in formulations (continuation)

Technique	Experimental details	Linear range (mg L ⁻¹)	LOD (mg L ⁻¹)	Recovery (%)	Ref.
Spectrophotometry	Indirect quantification ^a using alkaline hydrolysis and derivatization	0.2-10	0.028	95.0-99.0	15
Micellar liquid chromatographic	Direct quantification	1-20	0.03	-	9
Spectrophotometry and amperometry in flow-injection analysis (FIA) systems	Indirect quantification ^a using alkaline hydrolysis and derivatization	0.02-2.0	0.002	97-102	13

^aIndirect quantification means that carbaryl underwent hydrolysis and/or derivatization to be quantified.

Conflicts of interest

The authors declare no conflict of interest.

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SUPPLEMENTARY MATERIAL

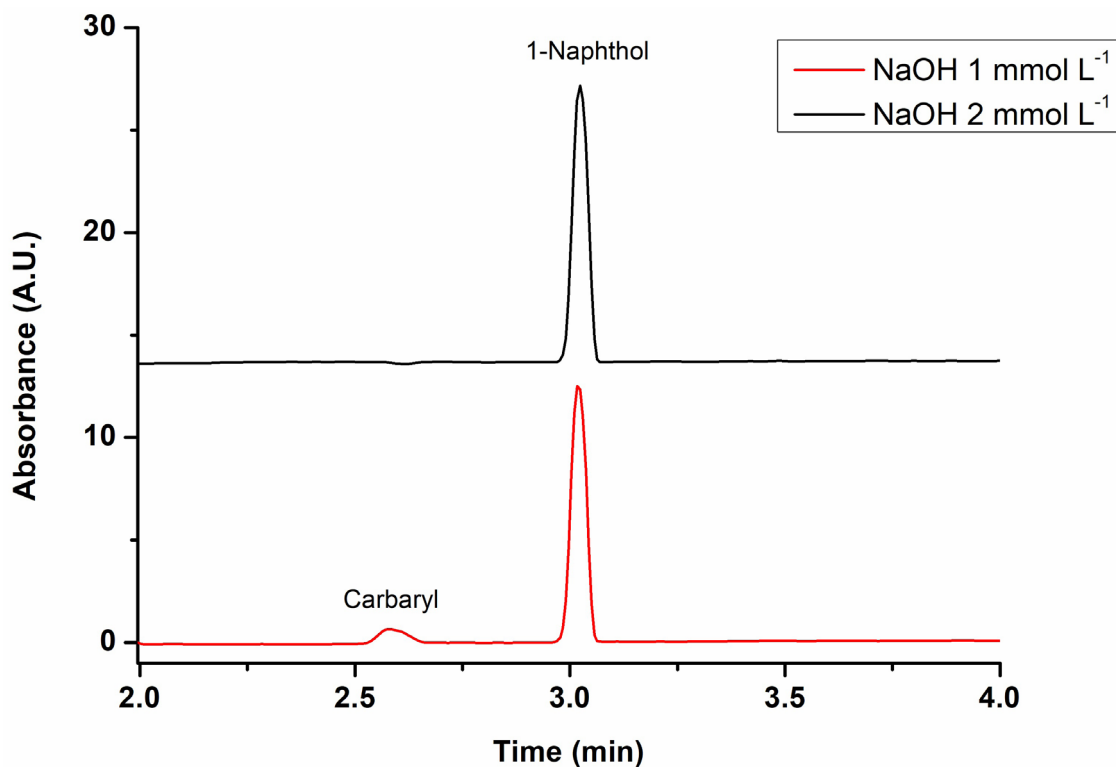


Figure S1. Electropherograms of standard solutions of carbaryl (40 mg L^{-1}) after 10 min of alkaline hydrolysis with NaOH concentrations of 1 and 2 mmol L^{-1} . Separation conditions: BGE: 10 mmol L^{-1} sodium borate buffer (pH 9.3); bare fused silica capillary with a total length of 60 cm (52 cm, effective) and $50 \text{ }\mu\text{m}$ i.d.; hydrodynamic sample injection for 5 s at 50 mbar; separation voltage of 25 kV; spectrophotometric detection at 214 nm.