Brazilian Journal of Analytical Chemistry
2025, Volume 12, Issue 48, pp 158-169
doi: 10.30744/brjac.2179-3425.AR-21-2024

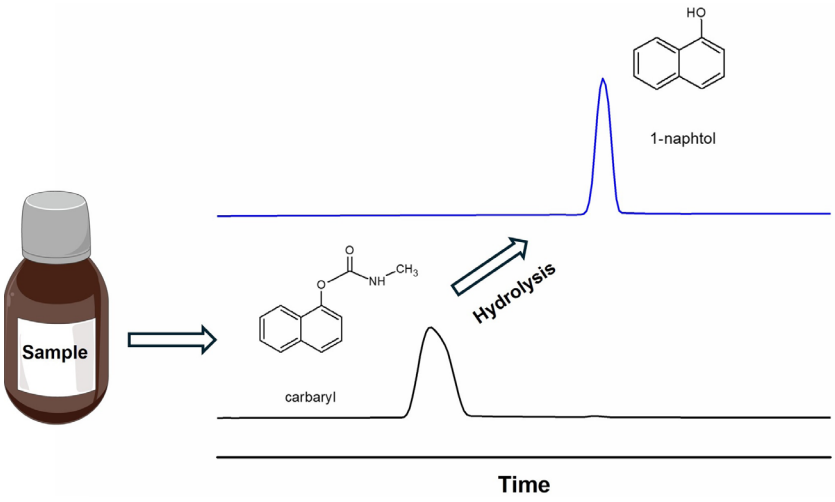
BrJAC

ARTICLE

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

Natalia Milaneze Cardoso, Bruna Kethelyn Pereira, José Alberto Fracassi da Silva, Dosil Pereira de Jesus*

Instituto de Química, Universidade Estadual de Campinas – UNICAMP, P.O. Box 6154, 13083-970 Campinas, SP, Brazil



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 (R^2) 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

Cite: Cardoso, N. M.; Pereira, B. K.; da Silva, J. A. F.; de Jesus, D. P. Simple and Fast Determination of Carbaryl Pesticide in Commercial Topical Formulations by Capillary Electrophoresis. *Braz. J. Anal. Chem.* 2025, *12* (48), pp 158-169. http://dx.doi.org/10.30744/brjac.2179-3425.AR-21-2024

Submitted February 21, 2024, Resubmitted May 25, 2024, Accepted June 7, 2024, Available online June 13, 2024.

This article was submitted to the BrJAC special issue celebrating the achievement of Journal Impact Factor.

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]

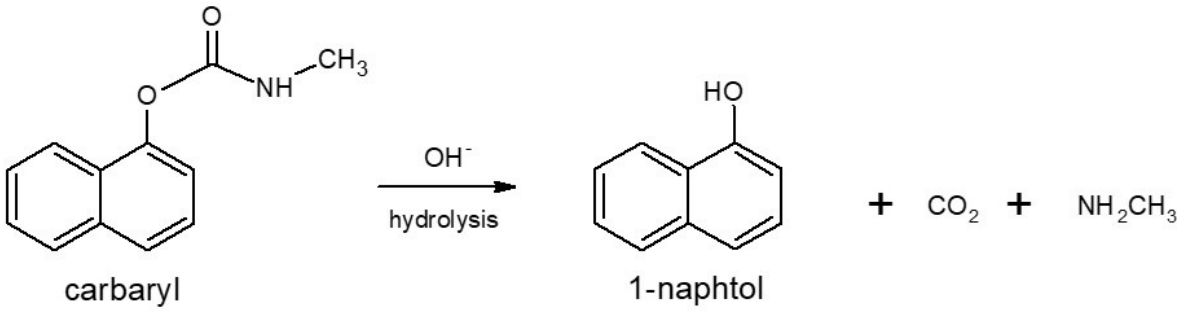


Figure 1. Alkaline hydrolysis reaction of carbaryl.

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 $Na_2B_4O_7.10H_2O$ (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 (4º 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 (R^2) from the linear regression and a lack of fit test[28] 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.

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

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 μmol 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 μmol 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.

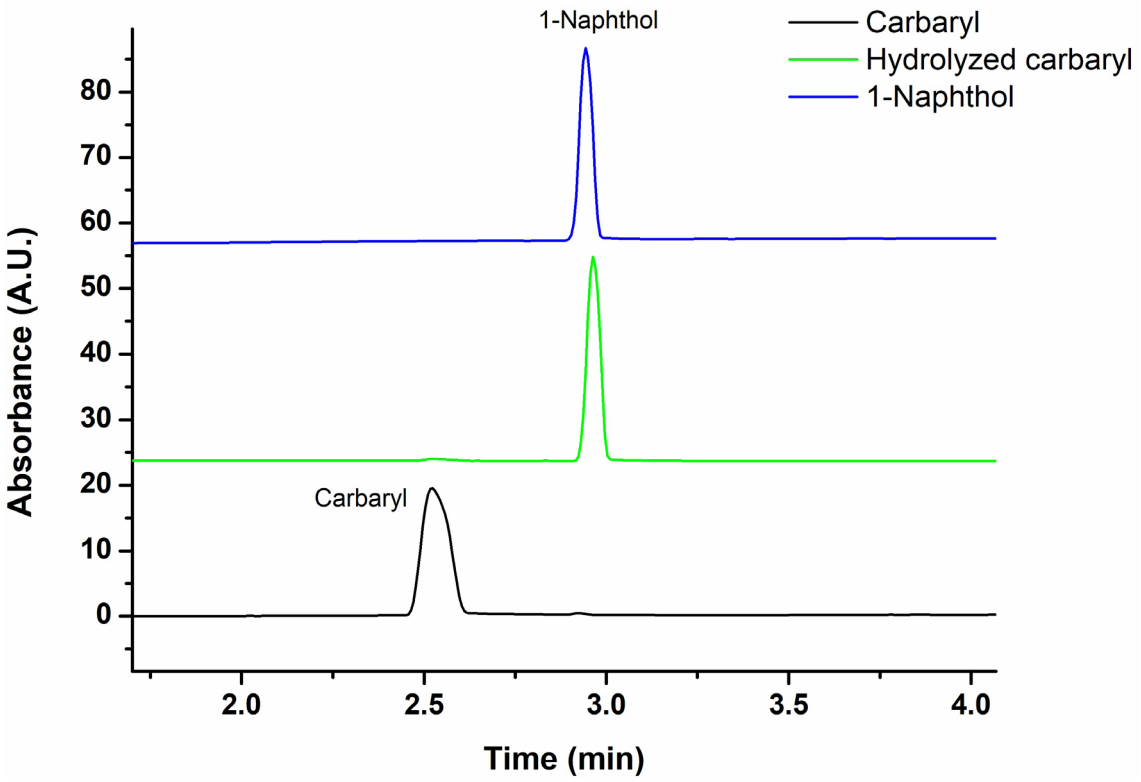


Figure 2. Electropherograms of standard solutions of carbaryl (40 mg L^{-1}) without hydrolysis, 1-naphthol (200 µmol L^{-1}), and carbaryl (40 mg L^{-1}) after alkaline hydrolysis (2 mmol L^{-1} NaOH). Separation conditions: BGE: 10 mmol L^{-1} sodium borate buffer (pH 9.3); bare fused silica capillary with a total length of 60 cm (52 cm, effective) and 50 µm 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-value $< F_{tab}$ (2.74) and P-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

(continues on next page)

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

[a]Mean ± standard deviation for 7 consecutive replicate runs; [b]Number of plates per meter; [c]calibration curve obtained in triplicate (n = 3); [d]95% significance level; [e]Limits 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 ± 4
	20	22	110 ± 7
	30	30.9	103 ± 3
Powder 2	10	9.4	94 ± 6
	20	17	85 ± 6
	30	27.3	91 ± 7
Powder 3	10	9.0	90 ± 6
	20	19.8	99 ± 7
	30	24.9	83 ± 2
Dry bath gel	0.25	0.20	82 ± 2
	0.50	0.40	80.0 ± 0.5
	0.75	0.60	80 ± 1

[a]n = 3

Application of the CZE method

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

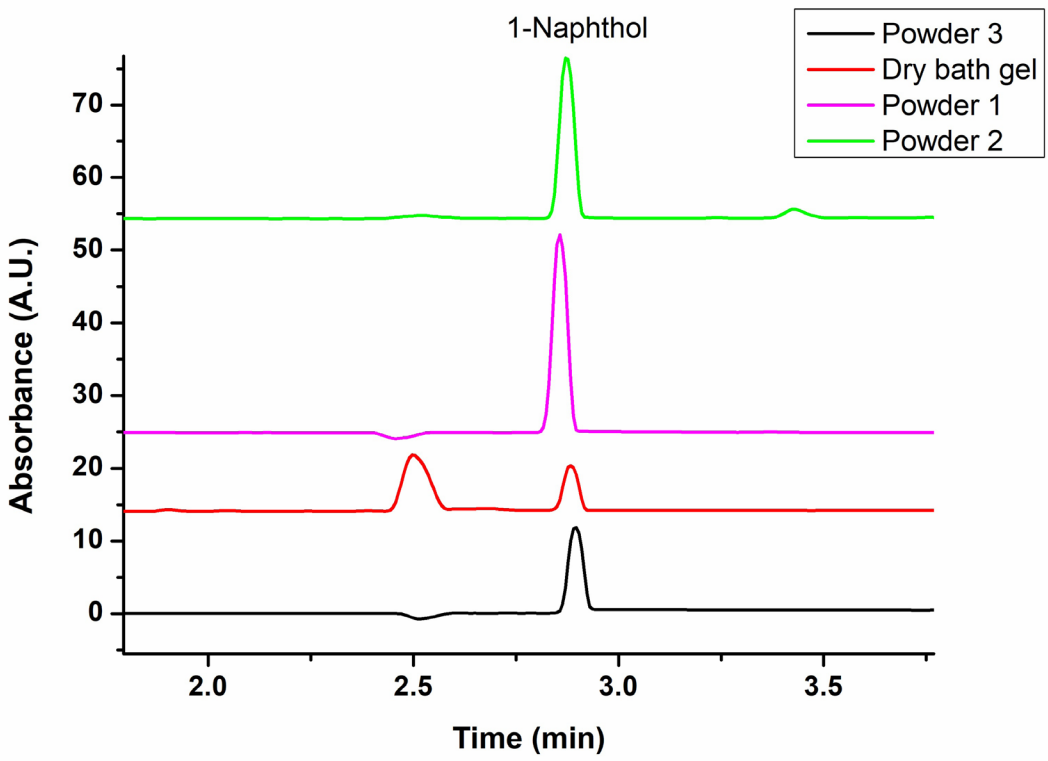


Figure 3. Electropherograms of the analyzed samples of commercial topical formulations containing carbaryl. Separation conditions as in Figure 2.

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

[a]informed by the manufacturer; [b]n = 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

(continues on next page)

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

[a]Indirect quantification means that carbaryl underwent hydrolysis and/or derivatization to be quantified.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors acknowledge the financial support provided by the “Fundação de Amparo à Pesquisa do Estado de São Paulo” (FAPESP) [grant # 2023/14915-2] and the “Instituto Nacional de Ciência e Tecnologia em Bioanalítica” [FAPESP/INCT-Bio grant #2014/50867-3], and the “Serviço de Apoio ao Estudante” (SAE-Unicamp).

REFERENCES

(1) Gunasekara, A. S.; Rubin, A. L.; Goh, K. S.; Spurlock, F. C.; Tjeerdema, R. S. Environmental Fate and Toxicology of Carbaryl. In: Whitacre, D. (Ed.) *Reviews of Environmental Contamination and Toxicology*, vol 196. Springer, New York, NY., 2008, pp 95–121. https://doi.org/10.1007/978-0-387-78444-1_4

(2) Lima, M. P. R.; Cardoso, D. N.; Soares, A. M. V. M.; Loureiro, S. Carbaryl Toxicity Prediction to Soil Organisms under High and Low Temperature Regimes. *Ecotoxicol. Environ. Saf*. **2015**, *114*, 263–272. https://doi.org/10.1016/j.ecoenv.2014.04.004

(3) United State Dept. of Agriculture (USDA), Plant Protection and Quarantine-Policy Management, Animal and Plant Health Inspection Service. *Final Human Health and Ecological Risk Assessment for Carbaryl Rangeland Grasshopper and Mormon Cricket Suppression Applications,* 2019. Available at: https://www.aphis.usda.gov/plant_health/ea/downloads/2019/carbaryl-hhera-final.pdf (accessed on 14 February 2024).

(4) Kumar, S.; Baggi, T. R.; Al-Zughaibi, T. Forensic Toxicological and Analytical Aspects of Carbamate Poisoning – A Review. *J. Forensic. Leg. Med.* **2022**, *92*, 102450. https://doi.org/10.1016/j.jflm.2022.102450

(5) Jing, X.; Wang, H.; Huang, X.; Chen, Z.; Zhu, J.; Wang, X. Digital Image Colorimetry Detection of Carbaryl in Food Samples Based on Liquid Phase Microextraction Coupled with a Microfluidic Thread-Based Analytical Device. *Food Chem.* **2021**, *337*. https://doi.org/10.1016/j.foodchem.2020.127971

(6) Hawker, D. Kinetics of Carbaryl Hydrolysis: An Undergraduate Environmental Chemistry Laboratory. *J. Chem. Educ.* **2015**, *92* (9), 1531–1535. https://doi.org/10.1021/acs.jchemed.5b00097

(7) Liu, C.; Cao, Y.; Zhao, T.; Wang, X.; Fang, G.; Wang, S. A Novel Multi-Purpose MIP for SPE-HPLC and QCM Detection of Carbaryl Residues in Foods. *Food Anal. Methods* **2021**, *14*, 331–343. https://doi.org/10.1007/s12161-020-01875-4

(8) Sun, B.; Wang, C.; Wang, Q.; Chen, L.; Dang, X.; Huang, J.; Chen, H. Preparation of Acryloyl β-Cyclodextrin Organic Polymer Monolithic Column and Its Application in Solid-Phase Microextraction and HPLC Analysis for Carbofuran and Carbaryl in Rice. *Food Anal. Methods* **2017**, *10* (12), 3847–3855. https://doi.org/10.1007/s12161-017-0931-1

(9) Gil-Agustí, M.; Alvarez-Rodríguez, L.; Monferrer-Pons, L.; Bose, D.; Durgbanshi, A.; Esteve-Romero, J. Chromatographic Determination of Carbaryl and Other Carbamates in Formulations and Water Using Brij-35. *Anal. Lett.* **2002**, *35* (10), 1721–1734. https://doi.org/10.1081/AL-120013051

(10) Somboon, T.; Santaladchaiyakit, Y.; Sansuk, S.; Srijaranai, S. An Alternative Spectrophotometric Determination of Carbaryl Insecticide Residues in Water Samples Using the Cerium-Catalyzed Belousov-Zhabotinsky Oscillating Reaction. *J. Braz. Chem. Soc.* **2020**, *31* (5), 963–970. https://doi.org/10.21577/0103-5053.20190261

(11) Didpinrum, P.; Ponhong, K.; Siriangkhawut, W.; Supharoek, S. ang; Grudpan, K. A Cost-Effective Spectrophotometric Method Based on Enzymatic Analysis of Jackfruit Latex Peroxidase for the Determination of Carbaryl and Its Metabolite 1-Napthol Residues in Organic and Chemical-Free Vegetables. *Food Anal. Methods* **2020**, *13* (2), 433–444. https://doi.org/10.1007/s12161-019-01667-5

(12) Manjubhashini, A. B.; Raman, G. K.; Kumar, A. S. Spectrophotometric Determination of Carbaryl in Its Formulations, Waters and Food Grains. *Int. J. Food Sci. Technol.* **2003**, *38* (6), 741–743. https://doi.org/10.1046/j.1365-2621.2003.00730.x

(13) Portela, D. C.; Pereira, I. M. F.; Paíga, P.; Delerue-Matos, C.; Vaz, M. C. V. F. Amperometric and Spectrophotometric Determination of Carbaryl in Natural Waters and Commercial Formulations. *Anal. Bioanal. Chem.* **2003**, *377* (2), 356–361. https://doi.org/10.1007/s00216-003-2107-7

(14) Sharma, D. K.; Dharmani, T.; Sharma, N. Extractive Spectrophotometric Method for the Determination of Carbaryl in Environmental Samples. *Bull. Chem. Soc. Ethiop*. **2015**, *29* (2), 173–186. https://doi.org/10.4314/bcse.v29i2.2

(15) Rekha, D.; Suvardhan, K.; Kumar, K. S.; Jayaraj, B.; Chiranjeevi, P. Analysis of Carbaryl Pesticide Residues in Environmental Samples with Spectrophotometry. *Chin. J. Chem.* **2006**, *24* (8), 1095–1100. https://doi.org/10.1002/cjoc.200690204

(16) Kumar, K. S.; Suvardhan, K.; Chiranjeevi, P. Preparation of Reagents for the Sensitive Spectrophotometric Determination of Carbaryl in Environmental Samples. *Anal. Lett.* **2005**, *38* (4), 697–709. https://doi.org/10.1081/AL-200050334

(17) Chen, Y.; Wu, H. L.; Wang, T.; Sun, X. D.; Liu, B. B.; Chang, Y. Y.; Chen, J. C.; Ding, Y. J.; Yu, R. Q. Quantitative Analysis of Carbaryl and Thiabendazole in Complex Matrices Using Excitation-Emission Fluorescence Matrices with Second-Order Calibration Methods. *Spectrochim. Acta, Part A* **2022**, *264*. https://doi.org/10.1016/j.saa.2021.120267

(18) Saha, C.; Bhushan, M.; Singh, L. R. Pesticide Sensing Using Electrochemical Techniques: A Comprehensive Review. *J. Iran. Chem. Soc.* **2023**, *20* (2), 243–256. https://doi.org/10.1007/s13738-022-02666-w

(19) Jain, U.; Saxena, K.; Hooda, V.; Balayan, S.; Singh, A. P.; Tikadar, M.; Chauhan, N. Emerging Vistas on Pesticides Detection Based on Electrochemical Biosensors – An Update. *Food Chem.* **2022**, *371*, 131126. https://doi.org/10.1016/j.foodchem.2021.131126

(20) Ren, Z.; Zhou, X.; Gao, X.; Tan, Y.; Chen, H.; Tan, S.; Liu, W.; Tong, Y.; Chen, C. Rapid Detection of Carbamate Pesticide Residues Using Microchip Electrophoresis Combining Amperometric Detection. *Anal. Bioanal. Chem.* **2021**, *413*, 3017–3026. https://doi.org/10.1007/s00216-021-03237-3

(21) Ben Attig, J.; Latrous, L.; Zougagh, M.; Ríos, Á. Ionic Liquid and Magnetic Multiwalled Carbon Nanotubes for Extraction of N-Methylcarbamate Pesticides from Water Samples Prior Their Determination by Capillary Electrophoresis. *Talanta* **2021**, *226*. https://doi.org/10.1016/j.talanta.2021.122106

(22) Cheng, X.; Wang, Q.; Zhang, S.; Zhang, W.; He, P.; Fang, Y. Determination of four kinds of carbamate pesticides by capillary zone electrophoresis with amperometric detection at a polyamide-modified carbon paste electrode. *Talanta* **2007**, *71* (3), 1083–1087. https://doi.org/10.1016/j.talanta.2006.06.001

(23) Zhang, C.; Ma, G.; Fang, G.; Zhang, Y.; Wang, S. Development of a Capillary Electrophoresis-Based Immunoassay with Laser-Induced Fluorescence for the Detection of Carbaryl in Rice Samples. *J. Agric. Food Chem.* **2008**, *56* (19), 8832–8837. https://doi.org/10.1021/jf801645m
(24) Smirnova, A.; Shimura, K.; Hibara, A.; Proskurnin, M. A.; Kitamori, T. Pesticide Analysis by MEKC on a Microchip with Hydrodynamic Injection from Organic Extract. *J. Sep. Sci.* **2008**, *31* (5), 904–908. https://doi.org/10.1002/jssc.200700533
(25) Da Silva, C. L.; De Lima, E. C.; Tavares, M. F. M. Investigation of Preconcentration Strategies for the Trace Analysis of Multi-Residue Pesticides in Real Samples by Capillary Electrophoresis. *J. Chromatogr. A* **2003**, *1014* (1–2), 109–116. https://doi.org/10.1016/S0021-9673(03)00711-8
(26) Hernández-Borges, J.; Frías-García, S.; Cifuentes, A.; Rodríguez-Delgado, M. A. Pesticide Analysis by Capillary Electrophoresis. *J. Sep. Sci.* **2004**, *27* (12), 947–963. https://doi.org/10.1002/jssc.200401820
(27) Bol'shakova, D. S.; Amelin, V. G. Determination of Pesticides in Environmental Materials and Food Products by Capillary Electrophoresis. *J. Anal. Chem.* **2016**, *71* (10), 965–1013. https://doi.org/10.1134/S1061934816100026
(28) Araujo, P. Key Aspects of Analytical Method Validation and Linearity Evaluation. *J. Chromatogr. B* **2009**, *877* (23), 2224–2234. https://doi.org/10.1016/j.jchromb.2008.09.030
(29) *Validation of analytical Procedures: Text and methodology*. ICH Harmonised Tripartite Guideline. International conference on harmonization of technical requirements for registration of pharmaceuticals for human use, 2005. Available at: https://database.ich.org/sites/default/files/Q2%28R1%29%20Guideline.pdf (accessed on 23 May 2024).
(30) Sen, I.; Shandil, A.; Aggarwal, M.; Khandal, R. K. Simultaneous Determination by Gas Chromatography of Lindane and Carbaryl in Combined Formulations. *E-Journal of Chemistry* **2011**, *8* (1), 391–399. Available at: https://pdfs.semanticscholar.org/6e7c/620d5834ca6a870a85a273069060824d97aa.pdf (accessed on 23 May 2024).
(31) Pulgarín, J. A. M.; Molina, A. A.; López, P. F. Automatic Chemiluminescence-Based Determination of Carbaryl in Various Types of Matrices. *Talanta* **2006**, *68* (3), 586–593. https://doi.org/10.1016/j.talanta.2005.04.051

SUPPLEMENTARY MATERIAL

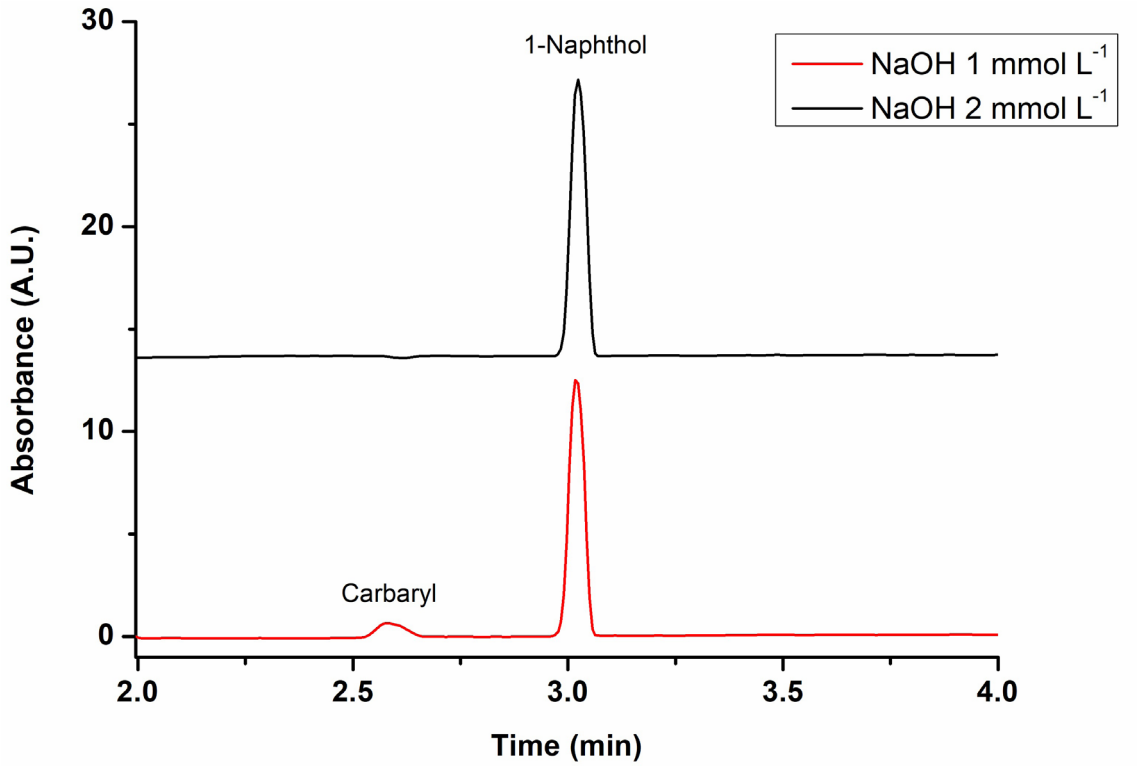


Figure S1. Electropherograms of standard solutions of carbaryl (40 mg L^{-1}) after 10 min of alkaline hydrolysis with NaOH concentrations of 1 and 2 mmol L^{-1}. Separation conditions: BGE: 10 mmol L^{-1} sodium borate buffer (pH 9.3); bare fused silica capillary with a total length of 60 cm (52 cm,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