Analysis of Phenoxyl-Type *N*-Methylcarbamate Pesticide Residues in Vegetables by Capillary Zone Electrophoresis with Pre-Column Hydrolysis and Amperometric Detection

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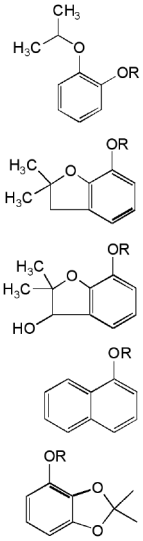
Abstract

With systematic studies of pre-column thermal hydrolysis, a method is described for the determination of five phenoxyl-type *N*-methylcarbamates (NMCs) (viz., propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb) in vegetables by capillary zone electrophoresis with amperometric detection. Effects of hydrolysis parameters such as alkali medium, temperature, and hydrolysis time, as well as separation conditions, are investigated. Under the optimum conditions, baseline separation of five hydrolysates is achieved within 16 min. Good calibration curves of propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb are obtained from 1.20×10^{-7} to 5.00×10^{-5} mol/L, and their detection limits (S/N = 3) are 1.80×10^{-8}, 1.50×10^{-8}, 1.80×10^{-8}, 2.50×10^{-8}, and 1.80×10^{-8} mol/L, respectively, which is approximately 20~50-fold more sensitive than those previously reported with a UV method. In the application of vegetable samples, the five NMCs are well determined. Average recoveries of 75~89% and 86~100% at fortified levels of 0.05 and 0.80 mg/kg are achieved with relative standard deviations of 2~6%, respectively. The method is sensitive, reproducible, and provides an alternative means for the analysis of phenoxyl-type NMC pesticide residues.

Introduction

N-methylcarbamates (NMCs) have been widely used for pest control due to their effectiveness and broad spectrum of biological activity. Because most NMCs are acutely toxic, their residues in foodstuffs have a potential hazard to the health of consumers (1–2). As a result, it is necessary to establish a simple, sensitive method for the determination of NMC residues in vegetables.

Many analytical methods have been developed for the determination of NMCs and their metabolites in the foodstuffs. NMC pesticides are thermally labile and not amenable to gas chromatography (3–4). High-performance liquid chromatography (HPLC) is preferable and often used to monitor NMCs with various detectors (5–9). Currently, the hyphenated techniques such as HPLC–fluorescence and HPLC–mass spectrometry (MS) offer the prevailing schemes for the determination of residual pesticides, due to their specific identification, good selectivity, and sensitivity (10–11). It should be pointed out that MS instruments are quite costly. Usually the post-column fluorescence detection of pesticides is achieved using relatively complicated equipment, though efforts have been devoted to simplifying the instrumental setup by de Kok, Hiemstra, and Nondek et al. (11). Recently, alternative and complementary methods, using much simpler capillary electrophoresis (CE), have emerged in pesticide analysis (12–13). The prospects of CE are quite promising due to its advantages of high separation efficiency, simple manipulations, and very small consumption of toxic solvents (14–15). It is a cleaner and more convenient method. The applications of the CE technology to pesticide analysis have been receiving more



NMC pesticide R=CONHCH$_3$	Hydrolytic metabolites R=H
Propoxur	2-Isopropoxyphenol
Carbofuran	3,3-Dihydro-2,2-dimethyl--7-benzofuranol
Carbofuran-3-hydroxy	3-hydroxy-2,2-dimethyl--7-benzofuranol
Carbaryl	1-Naphthol
Bendiocarb	2,3-(isopropylidenedioxy) phenol

Figure 1. Structures and common names of the NMCs and hydrolysates studied in this work.

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and more attention (16–17). With regard to NMC residues, micellar electrokinetic capillary chromatography (MECC) has been the main means in recent publications (11,16–18).

So far, numbers of detection modes coupled with CE (e.g., MECC) have been used for NMC pesticides, such as UV or diode-array (18), fluorescence (11), and MS (19). Although the UV or diode-array detector is common and easy to handle, an enrichment must precede the separation to solve the intrinsic drawback of low sensitivity. Fluorescence detection acts as an acceptable method because it is sensitive and selective; however, the extremely short optical path length in CE and the fluorescence derivatization of most NMCs may be potential disadvantages (11,20). An MS detector can solve the previously mentioned problems in the majority of applications, but it is too expensive. As an alternative sensitive detection mode, amperometric detection (AD) can offer many desirable features for CE systems due to its high sensitivity, low cost, and miniaturized instrumentation (20–21). However, it is not easy to determine the NMCs directly by capillary zone electrophoresis (CZE)–AD due to their inherently weak electroactivity.

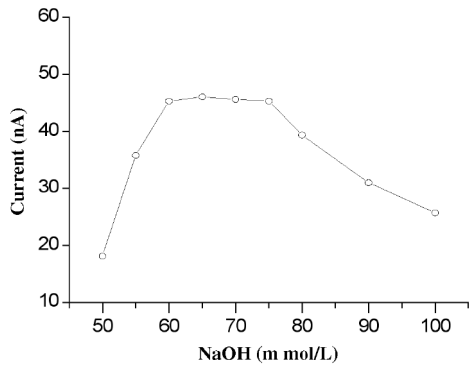

Figure 2. Effect of alkali concentration on pre-column hydrolysis. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; running solution, borate buffer (50 mmol/L, pH = 9.8); separation voltage, +21 kV; injection time, 10 s; working potential, + 0.85 V; hydrolysis time, 30 min; hydrolysis temperature, 40°C. Carbofuran, 2.00 × 10^{-5} mol/L.

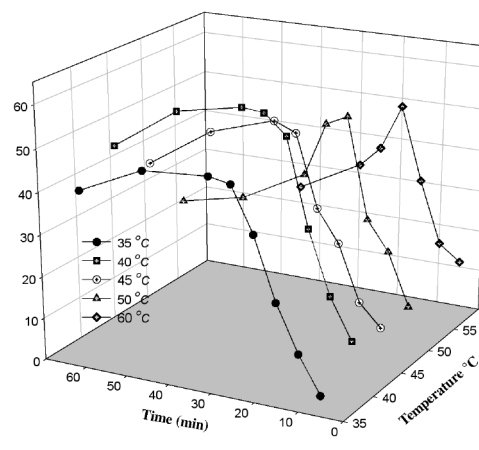

Figure 3. Effects of temperature and hydrolysis time on the peak current. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; buffer: borate buffer (50 mmol/L, pH = 9.8); separation voltage, +21 kV; injection time, 10 s; working potential, +0.85 V; carbofuran, 2.00 × 10^{-5} mol/L; alkaline, 65.0 mmol/L NaOH; hydrolysis times: 5, 10, 15, 20, 25, 30, 45, and 60 min, respectively.

Fortunately, with thermal hydrolysis, NMCs can be decomposed, and the resulting phenolic hydrolysates with high electroactivity can be obtained and detected sensitively in a CZE–AD method. A unique attempt of Fang's group (20) demonstrated the sensitive determination of four carbamates (fenobucarb, isoprocarb, etc.) by CZE–AD after a pre-column hydrolysis. This method was of high sensitivity, good reproducibility, and could be used in the rapid determination of the pesticide residues (20). However, information on the thermal hydrolysis behavior of NMCs was not expatiated. To our knowledge, the detailed studies of thermal hydrolysis and the sensitive detections of typical phenoxyl-type NMCs (propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl and bendiocarb) in vegetables by CZE–AD have not been reported.

In this report, with a systemic study of pre-column thermal hydrolysis, a CZE–AD scheme was presented and applied to the determination of the five phenoxyl-type NMCs in vegetables. Effects of NaOH, temperature and hydrolysis time, acidity and concentration of running buffer, and separation voltage were optimized. In addition, the applications to the analysis of five NMCs in vegetables were also evaluated at fortified levels of 0.05 and 0.80 mg/kg. Based on the method developed, the information on the hydrolysis behavior was gained and the five NMCs were well analyzed with detection limits of 10^{-8} mol/L.

Experimental

Apparatus and reagents

The CZE–AD system was laboratory-built. The CZE separation was performed in a fused-silica capillary (80 cm × 25 µm i.d. × 375 µm o.d. Hebei Yongnian, China). NMCs were injected electrokinetically at a certain applied voltage for 10 s with a ± 30 kV high-voltage power supply (Shanghai Institute of Applied Physics, CAS, China). The wall-jet amperometric detection was carried out in a three-electrode cell system which consisted of a 300 µm diameter carbon disc-working electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode. An LC-3D potentiostat (BAS, West Lafayette, IN) was used to control the

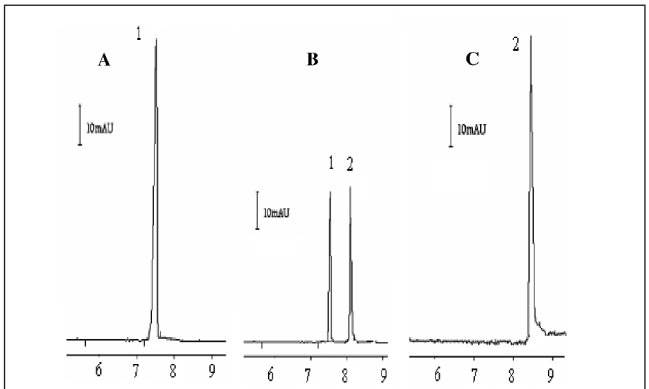

Figure 4. Electropherograms of carbofuran and its hydrolysate at different hydrolysis time with UV detection. Experimental conditions: carbofuran, 2.00 × 10^{-5} mol/L; alkaline, 0.065 mol/L NaOH; UV detection, 220 nm; separation voltage: 20 kV; borate buffer, 50.0 mmol/L + SDS (10 mmol/L), pH = 9.8. Carbofuran, 2.00 × 10^{-5} mol/L; 0 (A); 15 min (B); 30 min (C).

potential and measure the current. All the data collections of CZE–AD system were performed using a chromatographic workstation system (Zhejiang University, China). A CHI660 electrochemical system (CHI Instruments, Austin, TX) was used for cyclic voltammograms.

All chemicals were of analytical reagent grade. All solutions were prepared with deionized water. Propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb were purchased from Sigma (St. Louis, MO). The stock solutions of five NMCs with a concentration of 5.00×10^{-4} mol/L were prepared in methanol and stored at 4ºC. Running buffer was prepared with a solution of $Na_2B_4O_7.10H_2O$ and H_3BO_3. All the solutions were filtered through a 0.22-µm polypropylene acrodisc syringe filter and sonicated to remove bubbles.

Sample preparation

Vegetable samples were prepared as follows. Twenty-five grams of fresh vegetable was prepared and spiked with NMCs at a certain concentration. Fifty milliliters of ACN were added and the mixture was stirred for 2 min. Sequent centrifugation was processed for 5 min at 4000 rpm. Five milliliters of ACN upper extract were collected and dried under nitrogen at 70ºC. The vegetable samples were prepared in 0.50 mL NaOH medium for further procedures.

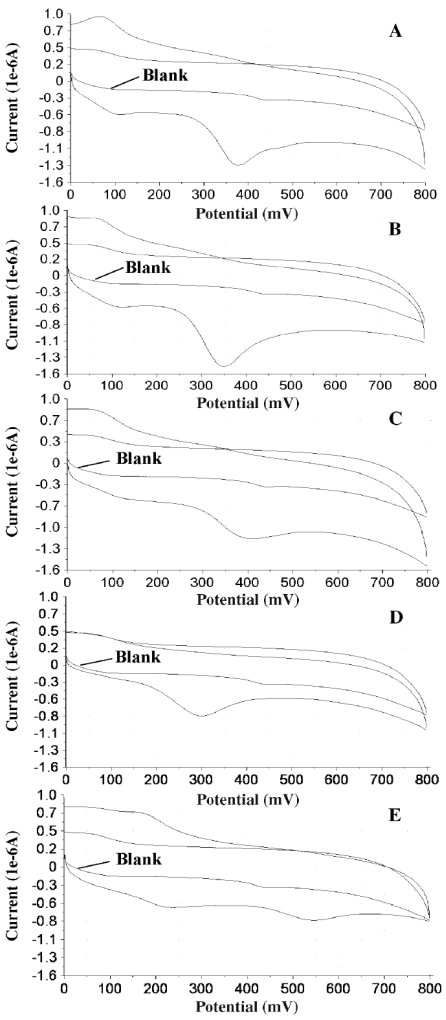

Figure 5. Cyclic voltammograms of five hydrolysis metabolites of NMCs. Experimental conditions: scan rate, 50 mV/s vs. Ag/AgCl; borate buffer, 50.0 mmol/L, pH = 9.8; working electrode, carbon electrode; NMCs, 2.00×10^{-4} mol/L. Propoxur (A); carbofuran (B); 3-hydroxy-carbofuran (C); carbaryl (D); bendiocarb (E).

Scheme for the analysis of NMCs

In a 65.0 mmol/L of NaOH medium, propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb were completely hydrolyzed at 40ºC for 30 min, and then sequent phenolic hydrolysates (Figure 1) were obtained after neutralization with 65.0 mmol/L of HCl. Through the use of the CZE–AD method, the resulting phenolic products of five NMCs were separated with borate buffer at pH 9.8, and detected sensitively at a carbon electrode with a detection potential of +0.85V. The indirect quantitative analysis of corresponding parent NMCs was available.

Procedure of CZE–AD

The capillary was sequentially rinsed with 0.10 mol/L NaOH and deionized water both for 5 min, followed by 10 min with a 50 mmol/L of borate buffer (pH = 9.8). The carbon disc electrode was successively polished with the emery paper and alumina powder, and then sonicated in water. NMC samples were injected electrokinetically at +21.0 kV for 10 s, and then separated at a separation voltage of +21.0 kV with a detection potential of +0.85 V (vs. Ag/AgCl).

Results and Discussion

Studies on the hydrolysis reaction

Initial experiments were devoted to finding the appropriate conditions for the hydrolysis of the phenoxyl-type NMCs. By using carbofuran as a representative, the effects of the concentration of sodium hydroxide were studied by CZE–AD over the range of 50.0~100.0 mmol/L. As shown in Figure 2, the maximal levels of the peak currents were achieved in 60.0~75.0 mmol/L, where the greatest yield of phenolic product was obtained. Besides, an obvious background noise causing a serious decrease

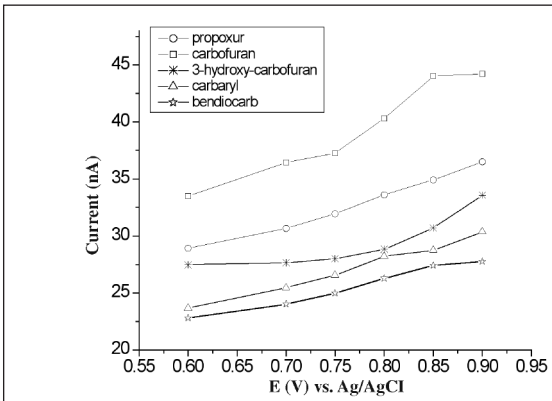

Figure 6. Hydrodynamic voltammograms of five hydrolysis metabolites. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; running solution, borate buffer (50.0 mmol/L, pH = 9.8); separation voltage, +21 kV; injection time, 10 s; NMCs, 2.00×10^{-5} mol/L.

of peak current could be observed when the alkali concentration increased from 75.0 to 100.0 mmol/L. On account of the stable and maximum peak height achieved, 65.0 mmol/L of NaOH was selected for further experiments.

Then the effect of hydrolysis time was studied from 5 to 60 min and the result is shown in Figure 3. At 40ºC, the current signal enhanced with increasing hydrolysis time to 30 min, and then levelled off when it was up to 45 min. Considering the compromise of peak current, stability, and analytical time, a hydrolysis time of 30 min was selected as optimal. Kinetic curves for the hydrolysis of NMCs were also plotted over the range of 35~60ºC. The highest yields of hydrolysis reaction were attained at the temperature of 40ºC in 30~45min. However, when the temperature increased to 50~60ºC, a decrease of peak height occurred and became more and more obvious, which might be due to the possible volatilization or further decomposition of phenolic products that go against the reliable detection. The optimization of the hydrolysis reaction was gained with 65.0 mmol/L of NaOH at 40ºC within 30 min.

Moreover, the yield of hydrolysis reaction in 65.0 mmol/L of NaOH at 40ºC with different hydrolysis times was also investigated by using a MECC-UV reference method, due to the electroneutrality of parent NMCs. As shown in Figure 4, at the beginning, carbofuran has not been hydrolyzed, and the unique peak of parent carbofuran was gained with migration time of 7.5 min (Figure 4A). With a hydrolysis time of 15 min, carbofuran was partly decomposed. The resulting phenolic product was obtained and indicated by the new peak with migration time of 8.1 min (Figure 4B). When the hydrolysis had been processed for 30 min, the peak of parent carbofuran disappeared and the peak of resulting phenolic product gained the maximum (Figure 4C), which indicated that carbofuran pesticide was completely dissociated.

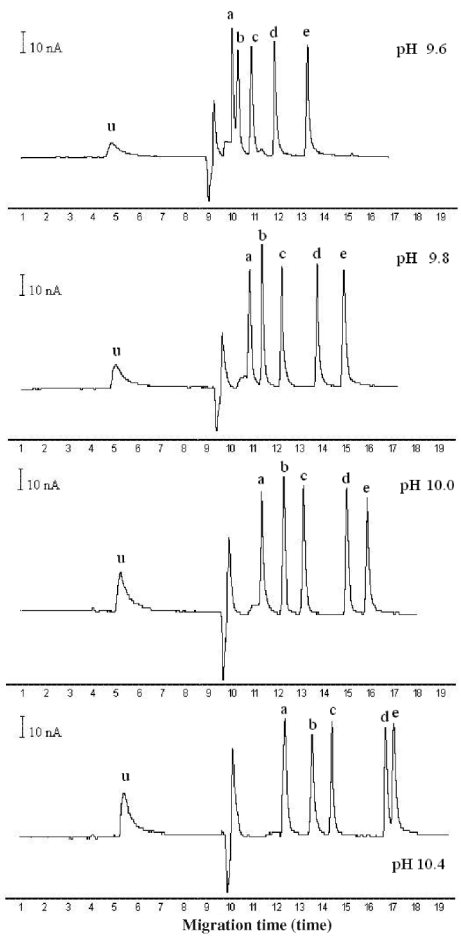

Figure 7. Effect of pH values on migration time. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; running solution, borate buffer (50.0 mmol/L); separation voltage, +21 kV; injection time, 10 s; working potential, +0.85V; NMCs, 2.00 × 10^{-5} mol/L. Peaks are: Propoxur (a); carbofuran (b); 3-hydroxy-carbofuran (c); carbaryl (d); bendiocarb (e); the peak of unknown substitute in CZE-AD (u).

Cyclic voltammetry and hydrodynamic voltammetry

Cyclic voltammograms of phenolic hydrolysates of five NMCs were investigated. The hydrolytic products were well oxidized and the anodic peaks were observable, although that of bendiocarb was relatively small. As shown in Figure 5, obvious oxidation peaks of hydrolytic products of NMCs such as propoxur, carbofuran, 3-hydroxy-carbofuran, and carbaryl were obtained at +0.30~+0.40 V (vs. Ag/AgCl) in a 50 mmol/L of borate buffer at pH 9.8, while the oxidation potential for the hydrolysate of bendiocarb was approximately +0.55 V.

Hydrodynamic voltammetry was also employed to optimize

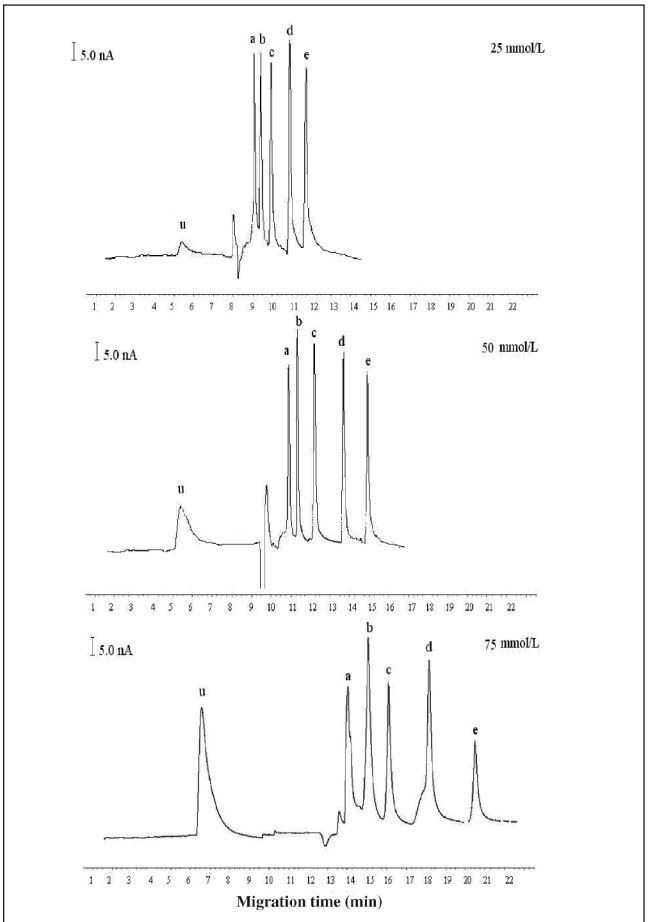

Figure 8. Effects of buffer concentrations. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; running solution, borate buffer (pH = 9.8); separation voltage, +21 kV; injection time, 10 s; working potential, +0.85 V; NMCs, 2.00 × 10^{-5} mol/L. Peaks: See Figure 7.

the detection potential (Figure 6). The oxidation currents of all five analytes increased rapidly with increasing potential up to +0.90 V (vs. Ag/AgCl). However, the baseline noise would increase obviously at a potential higher than +0.85V, which could go against the sensitive amperometric detection. So a detection potential of +0.85V was selected, at which the baseline was stable and the ratio of signal to noise (S/N) was maximum.

Effects of pH and concentration of buffer solution

The dependence of migration behavior of five hydrolysates on pH was studied in borate buffer over the pH range of 9.6~10.4. In such an alkali medium, phenolic hydrolysates were of negative charge, which led to reverse electrophoresis migration to the electroosmotic flow. With an increasing pH, the negative charge of phenolic products increased and the reverse action of electrophoresis was enhanced. The migration time of all hydrolysates was prolonged with an increase in pH (Figure 7). Satisfactory separation could be gained at a pH range of 9.8~10.0. The hydrolysate pairs such as propoxur and carbofuran, carbaryl and bendiocarb, could not be well separated at a pH of 9.6 or 10.4. At a pH value of 9.8, the best separation was achieved with an acceptable migration time within 16 min.

Figure 8 shows that the migration time and the resolution of five hydrolysates increased with buffer concentration ranging from 25.0 to 50.0 mmol/L at pH 9.8. However, with increasing buffer concentration to 75.0 mmol/L, a negative effect of Joule heating leading to a poor resolution became observable with the band broadening rising obviously, which might have led to a serious decrease of the resolution and the detection sensitivity. A 50.0 mmol/L of borate buffer with pH 9.8 was chosen. Besides, we noticed that there was some peak tailing in the CZE–AD detection. We assumed this might be mainly caused by the accurate alignment problem of the capillary with the electrode.

Effects of separation voltage and sample injection time

The effect of the separation voltage was investigated within the range from 15.0 to 24.0 kV. The migration times of the hydrolysates were significantly shortened and the corresponding current peaks were sharpened when the separation voltage was increased from 15.0 to 21.0 kV. However, a higher separation voltage at 22.0~24.0 kV could lead to an increase of baseline noise, resulting in peak broadening. An optimum voltage of 21.0 kV was chosen to accomplish a good analysis. It was found that peak current boosted up with an increase of the injection time, and leveled off with a severe band broadening when the injection time exceeded 10 s. The injection time of 10 s was selected as optimal.

Therefore, the optimum conditions of CZE–AD for indirect determination of the five NMCs were achieved. Figure 9 shows the electropherogram of five hydrolysates of standard NMCs. A baselined separation for the five hydrolysates was achieved within 16 min.

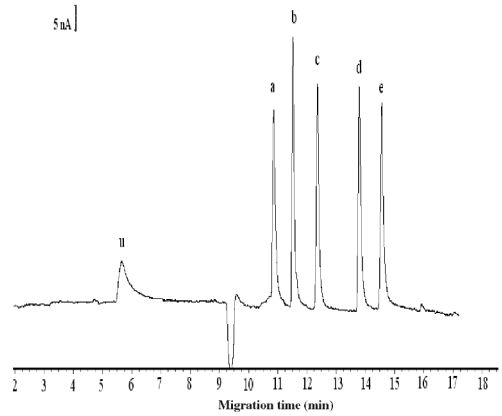

Figure 9. Electropherogram of the hydrolysate of standard NMCs. Experimental conditions: Capillary, 80 cm × 25 µm i.d. × 375 µm o.d.; running solution, borate buffer (50.0 mmol/L, pH = 9.8); separation voltage, +21 kV; injection time, 10 s; working potential, +0.85 V; NMCs: 2.00×10^{-5} mol/L of PRO, CAF, 3-OH-CAF, CAR, and BEN. Propoxur (a); carbofuran (b); 3-hydroxy-carbofuran (c); carbaryl (d); bendiocarb (e).

Reproducibility, linearity, and detection limits

A mixture of 2.00×10^{-5} mol/L propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb was analyzed. The relative standard deviations (R.S.D.) of peak current and migration time were ranging in 0.6~1.0% and 2.1~2.4%, respectively,

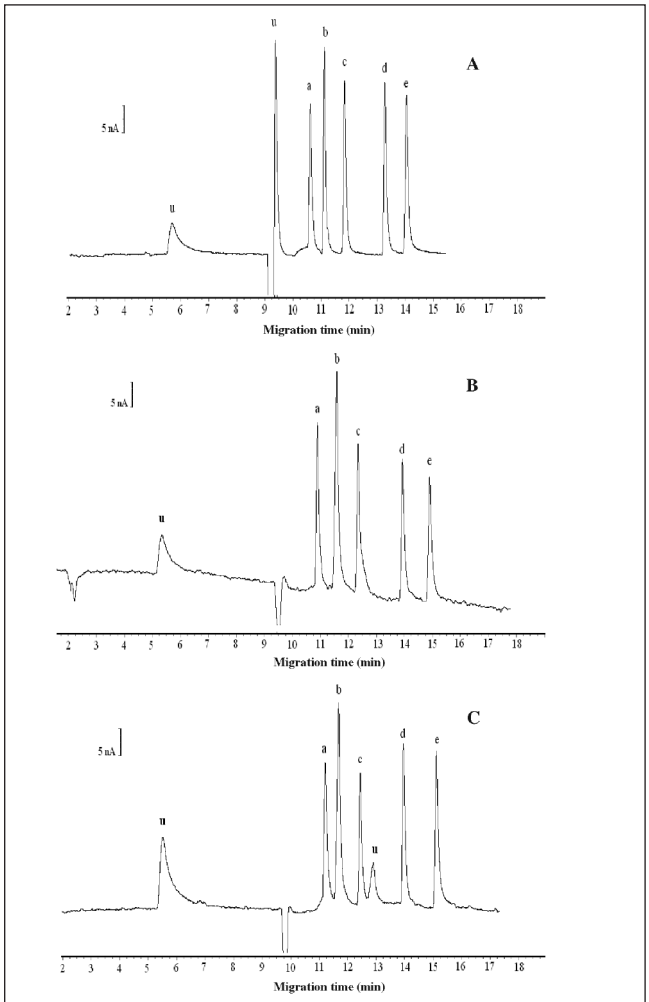

Figure 10. Electropherogram of the hydrolysate of fortified NMCs in vegetable samples. Experimental conditions were the same as in Figure 8. NMCs: 2.00×10^{-5} mol/L. Propoxur (a); carbofuran (b); 3-hydroxy-carbofuran (c); carbaryl (d); bendiocarb (e); the peak of unknown substitute in CZE-AD (u); cabbage (A); carrot (B); green pepper (C).

when the analysis was repeated five times under the same conditions.

A series of standard mixture of NMCs was tested. The calibration curves, regression equations, correlation coefficients, and detection limits are listed in Table I. The calibration curves exhibited satisfactory linearity over the concentration range of approximately three orders of magnitude. The detection limits (S/N = 3) were ranging from 1.50×10^{-8} to 2.50×10^{-8} mol/L. It was approximately 20~50-fold more sensitive than those with ultraviolet detection in vegetables.

Analytical application

Analysis of vegetable samples spiked with five phenoxyl-type NMCs (viz., propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb) was carried out to verify the applicability of this method. The chromatograms of carrot sample spiked with five NMCs at 0.80 mg/kg levels are shown in Figure 10. It showed that, in the fortified samples, five NMCs added into vegetables could be well detected without obvious disturbance of the coexisted pigment. Applied to the fortified vegetable samples (e.g., cabbage, carrot, and peppers), five NMCs fortified at 0.05 and 0.80 mg/kg were tested, and the method proven to be feasible. The recoveries were ranged from 75~89% and 86~100%, respectively (Table II). The R.S.D. were 2~6%. The results indicated that the CZE–AD with pre-column thermal hydrolysis could be applied to the analysis of NMCs in vegetables.

Table I. Results of Regression Analysis on Calibration Curves and Detection Limits

Ingredients	Regression equation $Y = aX + b$*	Correlation coefficient (r)	Linear range (mol/L)	Detection limit (mol/L)
Propoxur	$Y = 1.390X + 0.0897$	0.9989	$2.00 \times 10^{-7} – 5.00 \times 10–5$	1.80×10^{-8}
Carbofuran	$Y = 1.525X + 0.0595$	0.9986	$1.20 \times 10^{-7} – 5.00 \times 10–5$	1.50×10^{-8}
3-Hydroxy-carbofuran	$Y = 1.500X + 0.1710$	0.9998	$2.00 \times 10^{-7} – 5.00 \times 10^{-5}$	1.80×10^{-8}
Carbaryl	$Y = 1.156X + 0.1406$	0.9965	$1.70 \times 10^{-7} – 5.00 \times 10^{-5}$	2.50×10^{-8}
Bendiocarb	$Y = 1.425X + 0.1604$	0.9986	$1.40 \times 10^{-7} – 5.00 \times 10^{-5}$	1.80×10^{-8}

* Where the Y and X are the peak current (nA) and concentration of the analyte (μmol/L).

Table II. Recoveries of NMCs in Cabbages, Carrots, and Peppers*

Ingredients	Concentration (mg/kg)	Recovery, % (R.S.D., %, n = 3) Cabbages	Carrots	Peppers
Propoxur	0.80	91.1 (2)	91.8 (4)	87.3 (5)
	0.05	79.9 (3)	82.4 (3)	75.1 (5)
Carbofuran	0.80	87.5 (5)	95.8 (3)	86.0 (4)
	0.05	78.1 (4)	82.0 (5)	74.6 (6)
3-Hydroxy-carbofuran	0.80	100.3 (4)	91.7 (5)	87.0 (4)
	0.05	88.7 (4)	86.4 (3)	81.7 (6)
Carbaryl	0.80	88.6 (4)	92.2 (2)	96.6 (3)
	0.05	83.3 (2)	79.0 (5)	77.8 (6)
Bendiocarb	0.80	91.6 (2)	85.9 (6)	98.6 (5)
	0.05	84.6 (4)	81.5 (2)	84.9 (4)

* Experimental conditions are the same as in Figure 9.

Conclusion

A sensitive CZE-AD method with a systematic pre-column thermal hydrolysis was developed for the indirect analysis of five phenoxyl-type NMCs (propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb) via the determination of their phenolic products. The hydrolysates of five NMCs could be well separated within 16 min with good limits of detection at a level of 10^{-8} mol/L. It was more sensitive than the UV detection method reported previously by approximately 20~50-fold. This method was applied successfully to the determination of five NMCs in the extracts of vegetable samples, and good recoveries of propoxur, carbofuran, 3-hydroxy-carbofuran, carbaryl, and bendiocarb were achieved without obvious interferences of coexisted substances such as pigment. The recoveries at 0.05 and 0.80 mg/kg fortified levels were 75~89% and 86~100%, respectively, with RSD ranging from 2~6 %.

Acknowledgments

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