Electrochemical Detection of Carbamate Pesticides at Conductive Diamond Electrodes

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Conductive boron-doped diamond thin-film electrodes were used for the electrochemical detection of selected *N*-methylcarbamate pesticides (carbaryl, carbofuran, methyl 2-benzimidazolecarbamate, bendiocarb) after liquid chromatographic separation. Two kinds of detection methods were adopted in this study. In the first method, a direct detection of underivatized pesticides was carried out at an operating potential of 1.45 V versus Ag/AgCl, which resulted in the detection limits of 5–20 ng/mL (or 5–20 ppb) with S/N = 2 due to the low background current and wide potential window of the diamond electrode. In the second method, the detection limits were improved by subjecting the pesticide samples to alkaline hydrolysis in a separate step prior to injection. The phenolic derivatives obtained by alkaline hydrolysis oxidize at a relatively lower potential (0.9 V vs Ag/AgCl), which increases the sensitivity drastically. The advantage of the diamond electrode for the detection of phenolic derivatives is that it offers excellent stability in comparison to other electrodes. This method gives the detection limits of 0.6–1 ng/mL (or 0.6 –1 ppb), which are well below the maximum residue levels allowed for carbaryl, carbofuran, and bendiocarb. While the lowest detection limits (LOD) obtained by the direct detection of pesticides are comparable to the those reported by the well-established HPLC-fluorescence, the LODs of the alkaline hydrolysis method are found to be even lower than the reported limits. On-line reactivation of the diamond electrode surface was shown to be possible by an anodic treatment of the electrode at ∼3 V for 30 min in case of electrode fouling, which may occur after a prolonged use. Such a treatment damages the glassy carbon (GC) and metal electrodes, while the diamond electrode remains stable. These results suggest that the diamond electrode is superior to the other previously used electrodes such as GC and Kelgraf type for highly sensitive and stable detection of carbamate pesticides.

N-Methylcarbamates comprise an important class of pesticides widely used for the protection of a large varity of crops, and their residues may be encountered in fruits and vegetables. As the pesticides are unavoidable in modern life, the presence of their residues in foodstuffs poses a potential hazard for consumers due to their toxicity. For example, carbaryl, one of the carbamate pesticides, is known to cause nausea, vomiting, coma, and respiratory failure in humans.[1] The toxic effects of carbaryl and its major metabolite 1-naphthol are found to be due to the inhibition of cholinesterase and the teratogenic nature of these products.[1] Therefore, the maximum residue levels (MRLs) of pesticides in food samples are regulated by government agencies of most countries. For example, the MRLs for carbaryl, carboforon, and methiocarb are in 0.2–1.0 ppm range, depending on the particular pesticide/commodity combination.[2] The polarity and thermal instability of most *N*-methylcarbamates make their sensitive and accurate determination by gas chromatographic methods difficult. For this reason, numerous HPLC methods have been developed to analyze carbamates by UV spectrometry,[3,4] fluorometry,[2,5] or electrochemistry.[6–10] Although HPLC with a postcolumn derivatization and fluorescence detection method [U.S. Environmental Protection Agency (EPA) method 531.1][2] is sensitive and well established, it requires complex and expensive instrumentation. On the other hand, electrochemical methods offer both sensitivity and selectivity without the need of various-step derivatization procedures. They are simple and relatively inexpensive. Two kinds of electrochemical methods were previously used for the determination of these pesticides. First, a carbon-based Kelgraf composite electrode was employed for the detection of carbamates at high oxidation potentials.[6,7] The second method was based on the alkaline hydrolysis of these pesticides to produce phenolic derivatives which were then electrochemically detected at relatively lower potentials.[8–10]

In the case of the first method, which involves the direct detection of underivatized carbamate pesticides, the main practical problem is the high oxidation potentials of these pesticides where

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the oxygen evolution reaction interferes. The relatively high potential required for the detection of these pesticides strongly affects the detection limits, primarily due to the noise in the background current. In addition, because the high applied potentials allow less discrimination against interfering species, selectivity is lost. To improve the detection limits, Anderson and co-workers used Kelgraf electrodes that consist of graphite particles dispersed in an insulating Kel-F matrix.[6,7] These composite electrodes act as microarray-type electrodes. The recently emerged conductive diamond electrode appears to be very suitable for the analysis of these pesticides due to its high overpotential for the oxygen evolution reaction. The diamond electrode has been demonstrated to be much superior to the glassy carbon (GC) electrode for the detection of molecules that are oxidized at high potentials, e.g., histamine, caffeine, and azide.[11-13] In the present paper, we show the advantage of the diamond electrode for the detection of carbamate pesticides in terms of high sensitivity and long-term stability.

With a view toward improving detection limits and lowering the operational potential, Diaz et al.[10] hydrolyzed the carbamate pesticides to their corresponding phenolic derivatives, which was then followed by electrochemical detection at relatively lower potentials where the interference of oxygen evolution reaction is minimized. Although this method is very promising in comparison to the direct detection of underivatized pesticides, the major problem is electrode fouling as the phenol oxidation results in the formation of passive polymeric deposits on the electrode surface. In the electrochemical detection of phenolic compounds, GC is conventionally used as the electrode. However, rapid deactivation of this electrode is often observed.[9,14] In addition to the wide potential window, diamond has other superior qualities such as a low tendency for adsorption of neutral and polar chemical species, as well as low background current. Earlier, we showed the utility of diamond for the sensitive detection of NADH with high reproducibility in comparison to the GC electrode.[15] The electrogenerated NAD$^+$ strongly adsorbs on GC and causes electrode fouling, while diamond remains inert toward such adsorption. Likewise, Swain and co-workers demonstrated negligible adsorption of polar anthraquinonedisulfonate on diamond, while strong adsorption was observed on GC and defective HOPG.[16] Phenols are a class of compounds that cause electrode fouling after oxidation due to rapid polymerization of electrogenerated phenoxy radicals. However, recently, we succeeded in the detection of chlorophenols with high stability and sensitivity at the diamond electrode.[17] Here, we show the use of the diamond electrode for the stable detection of carbamate pesticides after hydrolysis to their phenolic derivatives, apart from the detection of underivatized pesticides.

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EXPERIMENTAL SECTION

Highly boron-doped diamond thin films were deposited by use of a microwave plasma chemical vapor deposition system (ASTeX, Woburn, MA), on silicon (100) wafers. Details of the deposition process have been reported elsewhere.[18] A mixture of acetone and methanol (9:1, v/v) was used as the carbon source, with dissolved B_2O_3 as the boron source. High-purity (99.99%) hydrogen gas was used as the carrier gas. The deposition of the film was carried out at a microwave power of 5 kW. A film thickness of $\sim$40 μm was achieved after 10 h of deposition. The Raman spectra of these films showed them to be of high quality, as evident from the strong characteristic peak at 1332 cm^{-1}.[18] The GC electrode (GC-30, Tokai Carbon Co., Ltd.) was pretreated by polishing with 1-mm alumina, followed by rinsing with high-purity water.

The flow injection analysis (FIA) and liquid chromatographic experiments were carried out with a micro-LC pump (BAS, LC-100), an injector (Rheodyne) with a 20-μL loop, a thin-layer flow cell (BAS), an amperometric detector (BAS LC-4C), and an $X-Y$ recorder (Graphtec, WX4000). The wall-jet-type flow cell consisted of the Ag/AgCl reference electrode and a stainless steel tube as the counter electrode, which also served as the tube for the solution outlet. The geometric area of the diamond electrode in the cell was estimated to be 0.64 cm^2. An Intersil CN-3 column (GL Science, 150 $\times$ 4.6 mm i.d.; particle size, 5 μm) and ODS columns were used for the separation of the pesticides. All the carbamate pesticides (analytical grade) were obtained from Wako. Phosphate buffer (pH 2.25)/acetonitrile was used as mobile phase for direct detection of underivatized pesticides. A mixture of acetic acid/water/acetoniile, 0.5%:59.5%:40%, was used as the mobile phase for the detection of prehydrolyzed pesticides (phenolic derivatives). All other reagents were analytical reagent grade. All solutions were prepared in Milli-Q water (Millipore).

RESULTS AND DISCUSSION

Direct Detection of Underivatized Pesticides. The voltammetric behavior of carbaryl at BDD and GC electrodes was examined in the phosphate buffer (pH 7.2). Figure 1 shows the voltammogram with nearly peak-shaped features at the diamond electrode whereas the voltammogram obtained at GC is featureless due to a large rising background current. The oxidation at the amide nitrogen in the carbamate molecule usually occurs at high oxidation potentials,[19] and the resulting voltammograms are sluggish at GC electrodes. However, due to its high overpotential for the oxygen evolution reaction, a relatively well-defined voltammogram is obtained for the diamond electrode. The voltammetric response is reproducible in the second and third cycles provided the solution is stirred after each cycle. Similar voltammograms were obtained for histamine,[11] caffeine,[12] and EDTA,[20] whose oxidation potentials are higher than 1.2 V versus SCE. For all these compounds on the diamond electrode, the signal-to-background (S/B) ratio was found to be 5−10 times higher than that of GC. The fact that inner-sphere reactions are relatively slow at the diamond electrode due to its poor adsorption capacity is the reason for the wide potential window.[21-23] Anodic oxygen

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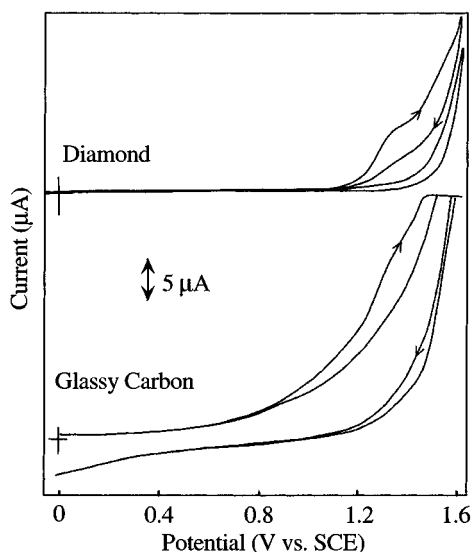(20) Sarada, B. V. Ph.D. Thesis, Tokyo University, 2000.

Figure 1. Cyclic voltammograms for 100 μM carbaryl in 0.1 M phosphate buffer (pH, 7.2) at diamond and glassy carbon electrodes. The lines without arrows indicate background voltammograms. The potential sweep rate was 0.1 V s^{-1}.

evolution and cathodic hydrogen evolution are typical inner-sphere reactions.

Figure 2 shows the hydrodynamic voltammograms obtained at two different pH values. When the pH was changed from 7.0 to 2.20, a positive shift of ~150 mV in the hydrodynamic voltammogram was observed. The hydrodynamic voltammogram obtained in acidic medium (pH 2.25) was more sigmoidally shaped in comparison to that obtained at neutral pH (Figure 2A) due to the anodic shift in the onset of oxygen evolution. The S/B ratio was also increased by 2.5 times (Figure 2B). It is pertinent to note that acidic medium was found to be better also in terms of reproducibility of the current response at the diamond electrode. The GC electrode exhibited a continuous increase in its background current after each measurement, even in acidic medium. The rotating disk electrode (RDE) experiments conducted in acidic medium have also shown highly reproducible sigmoidally shaped voltammograms under hydrodynamic conditions. A positive shift in the half-wave potential was found with increasing rotation rate, indicating partial kinetic control of the oxidation reaction. However, a plot of limiting current, I_{lim}, versus $\omega^{1/2}$ (the Levich plot) is linear, which shows that the reaction is transport limited at potentials more positive than the half-wave potential. Similar hydrodynamic voltammograms were obtained for carbofuran and bendiocarb, with nearly the same half-wave potential. In the case of methylbenzimidazole, the oxidation potential was lowered. It was probably due to the presence of the benzimidazole group. An operational potential of 1.45 V versus Ag/AgCl was selected for the pesticide determination, where the S/B ratio is maximum (Figure 2b). The calibration plots obtained at this potential were linear ($r = 0.999$) for all pesticides from 100 nM to 100 μM in flow injection mode (see Supporting Information).
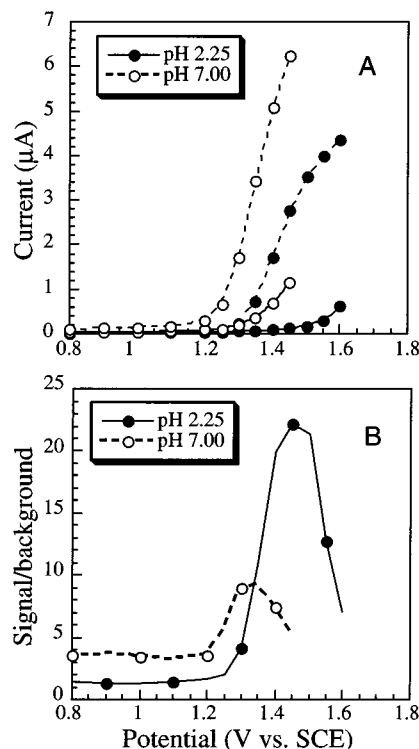
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Figure 2. Hydrodynamic voltammograms for 50 μM carbaryl at a diamond electrode at pH 2.25 and 7.2. The injection volume was 20 μL. The mobile phase was 0.1 M phosphate buffer. The flow rate was 1 mL min^{-1}.

It is noteworthy to mention here the superiority of the diamond electrode over GC in terms of stability of the background current. First, our previous studies indicated that the diamond electrode attains a stable background current level in a short time (10−15 min) even at moderate operational potentials (1 V vs Ag/AgCl).[24] Second, the background response continues to be stable even after 10 h of continuous operation at high operational potentials (above 1.2 V vs Ag/AgCl), whereas GC shows wide fluctuations and oxidative damage of the surface.[25] Diamond acts like a dimensionally stable anode,[26] while exhibiting attractive features that are useful for electroanalysis.

Figure 3 shows the chromatograms obtained for a pesticide mixture at high (20 μM) and low (200 nM) concentration levels. The complete separation of methyl 2-benzimidazolecarbamate, carbofuran, bendiocarb, carbaryl, and dichloron was achieved in the phosphate buffer (pH, 2.25) with 20% acetonitrile. This mobile-phase composition was optimized to achieve good separation. The first peak due to methylbendimidazole appears just after the solvent front. Although the peak height of this compound is higher than those of others, the peak completely disappears when it is analyzed in the low-concentration range (200 nM). Further optimization of the mobile-phase composition is necessary to overcome this problem. However, the other four pesticides could give well-defined peaks even at such low concentration. The noise

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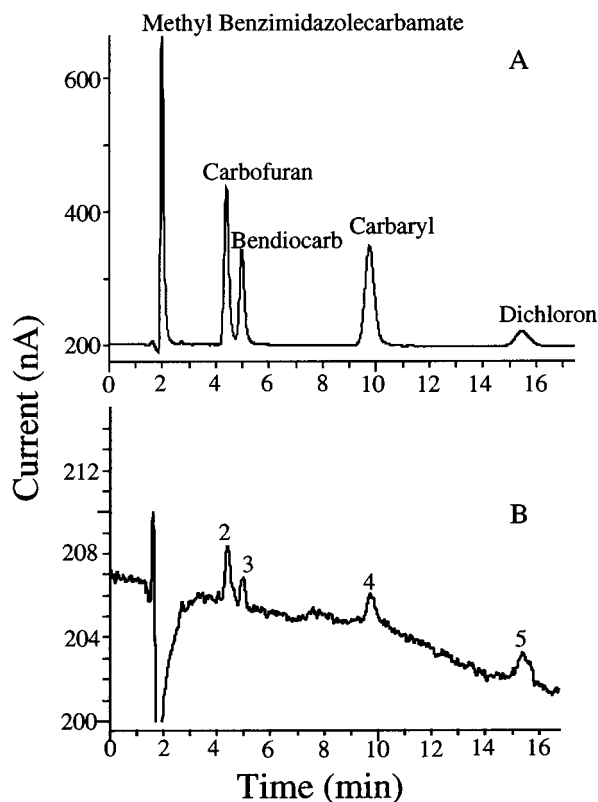
Figure 3. Chromatograms for (A) 20 μM standard carbamate pesticides (with 5 μM dichloron) and (B) 200 nM standard carbamate pesticides (with 50 nM dichloron). The applied potential was 1.45 V vs Ag/AgCl. The injection volume was 20 mL. The mobile phase was 0.1 M phosphate buffer (pH 2.25) with 20% acetonitrile.

at this operating potential was $\sim$500 pA. The detection limits (at S/N = 2) under these conditions are estimated to be 60, 100, 100, and 25 nM for carbofuran, bendiocarb, carbaryl, and dichloron, respectively. The stability of the electrode was tested for carbaryl detection in the flow injection mode. The response variation for 15 injections was estimated to be less than 2%, indicating excellent stability of the diamond electrode.

Detection of Pesticides after Alkaline Hydrolysis. The above method allows the direct detection of carbamate pesticides at a relatively high potential of 1.45 V, which shows less discrimination against interfering species in some cases. As mentioned before, the hydrolysis reaction to convert carbamates to their phenolic derivatives (Figure 4) is a promising approach that can minimize the interference problem, because phenols are more easily oxidizable than carbamates. Both precolumn and postcolumn hydrolysis techniques were applied to detect carbamates in their phenolic derivative forms. Diaz et al.[10] proposed a simple method where the hydrolysis of pesticides was performed in a prior separate step simply by adding sodium hydroxide at room temperature, which was then followed by the addition of acetic acid to adjust the pH. These prehydrolyzed samples were separated by isocratic elution, followed by electrochemical detection at the GC electrode. However, surface fouling causes problems in the electroanalysis of phenols. The electrochemically generated passive film is strongly adhered on the electrode surface. Washing with organic solvents is usually insufficient to regenerate the electrode activity. The film must be mechanically removed, for example, by polishing with diamond powder and

alumina powder slurries in ultrapure water on felt pads. Wang and Lin reported that repetitive electrochemical treatment can be used in situ to prevent solid electrode fouling in the presence of various deactivating compounds.[27] The optimal parameters for the electrochemical treatments of glassy carbon, however, are dependent on the electroactive reactants.

Figure 5A shows the cyclic voltammogram obtained for 50 μM carbaryl after hydrolyzing it to 1-naphthol. In the first scan (curve a), only one main anodic peak appeared at 0.7 V versus SCE, which is due to oxidation of 1-naphthol. However, new peaks appeared in the subsequent scans as shown in the second scan of the voltammogram (curve b). The new peaks are probably due to the oxidation products, naphthaquinone, and dihydroxynaphthalene. In a recent study, we obtained voltammograms for chlorophenol with similar features, and the additional peaks were found to be due to electrochemially generated hydroquinone and catechol.[17] Also, the anodic peak of naphthol in this study decreased in the second and subsequent scans, which is probably due to the adsorption of polynapthol, a polymer resulting from the naphthol oxidation. Such a behavior was reported for the oxidation of 2-naphthol at diamond electrodes.[28] However, rapid stirring of the solution after the first scan recovered the voltammogram, indicating that the adsorption is not permanent. It should be noted that a complete recovery is difficult after a few cycles. The scan rate dependence of peak current was examined by stirring the solution after each scan. The peak current was found to be linearly ($R = 0.997$) dependent on $v^{1/2}$ and a positive shift in the peak potential was observed with increasing scan rate, which indicated the irreversible nature of the reaction. Such scan rate dependence was not observed at the GC electrode.[9] Electrode fouling was observed after several scans without intermittent stirring of the solution. The blank (background) cyclic voltammogram for the fouled electrode showed an increase in the background current with broad features (Figure 5B, curve a). This is not usual for the diamond electrode because it is known for its inertness toward permanent adsorption of any chemical species. Our recent experience with chlorophenol detection at the diamond electrode is that it does not undergo fouling. From the present results, it is concluded that the adsorption of polynaphthol is stronger than that of polyphenol. However, the diamond electrode could be perfectly cleaned by treating it at the anodic potential of 2.5 V versus SCE for 10 min. At high anodic potentials, the diamond electrode produces hydroxyl radicals, which oxidatively destroy the polymer deposits, as demonstrated by Comninellis and co-workers.[28] The background voltammogram (Figure 5B, curve b) obtained after electrochemical treatment was similar to that of a fresh electrode (Figure 5A, curve c). The diamond electrode also gave a highly reproducible voltammogram for phenol oxidation similar to the first scan on a fresh electrode.

Figure 6A shows the hydrodynamic voltammograms at the diamond electrode for carbaryl, carbofuran, and bendiocarb after the prehydrolysis step. The mobile phase used was a solution of 0.01 M NaClO$_4$ in acetic acid/water/acetonitrile, 0.5%:59.5%:40%. The background current did not rise in the potential region where the phenolic derivatives of three pesticides exhibited oxidation. The derivative of carbaryl, 1-naphthol, oxidized much earlier than

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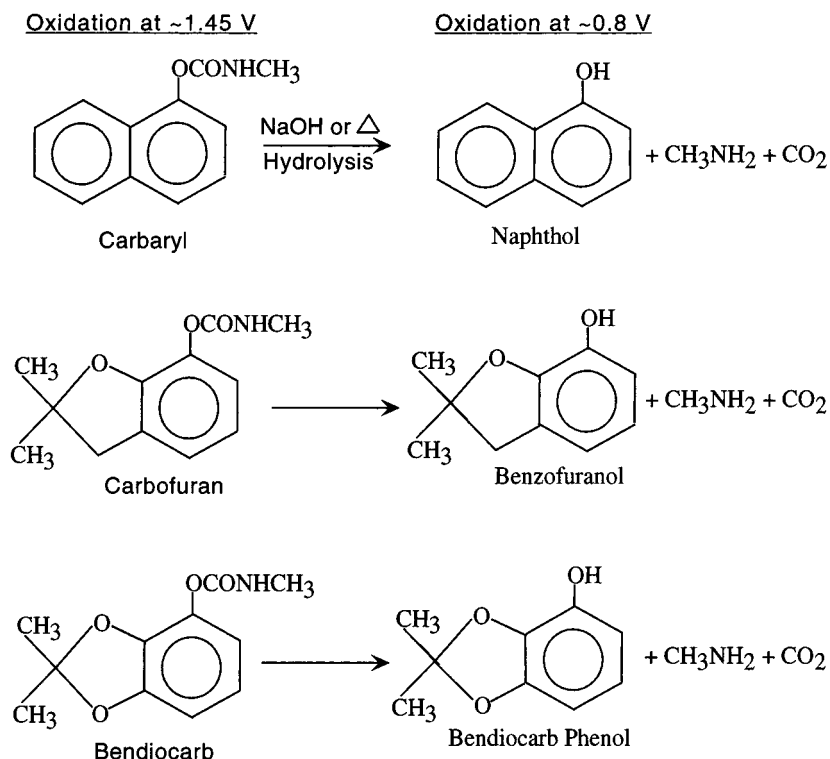
Figure 4. Scheme showing the hydrolysis of *N*-methylcarbamate pesticides to form their phenolic derivatives.
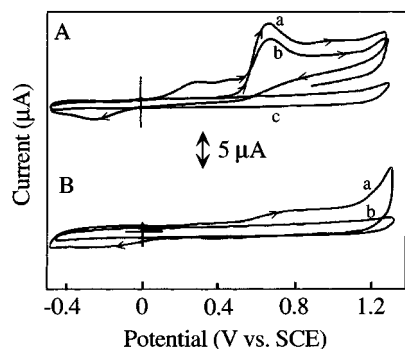

Figure 5. (A) Cyclic voltammograms for phenolic derivative (1-naphthol) of 50 μM carbaryl at a fresh diamond electrode in 0.1 M NaClO$_4$ containing 0.02 M NaOH. The pH was adjusted to 3.2 by adding glacial acetic acid. The potential sweep rate was 0.1 V s^{-1}: (a) first scan, (b) second scan, and (c) background. (B) Background voltammograms at used diamond electrode (a) before and (b) after electrochemical treatment at 2.5 V vs SCE for 10 min.

that of carbofuran and bendiocarn. The potential for the amperometric detection was set at 0.9 V versus Ag/AgCl, where all three pesticides give current responses.

The stability of the electrode response was tested for 50 μM carbaryl, whose phenolic derivative caused the deactivation of the diamond eletrode in cyclic voltammetric experiments performed in unstirred solutions. Figure 6B shows the amperometric response for repetitive 20-μL injections of 50 μM prehydrolyzed carbaryl. As expected, the response is very stable with a RSD of 2.5% for 10 injections. The degree of deactivation is expected to decrease in flow systems because the mobile phase carries electrogenerated products away from the electrode surface.[29] However, continuous operation may cause deactivation after
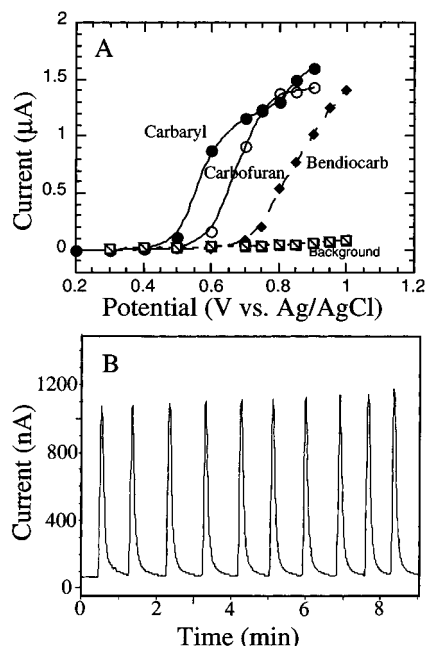
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Figure 6. (A) Hydrodynamic voltammograms for phenolic derivatives of 50 μM carbamates at diamond electrode. The injection volume was 20 μL. (B) FIA-ED results for diamond electrode using 20-μL injections of 50 μM prehyrolyzed carbaryl. Applied potential, 0.9 V vs Ag/AgCl. The mobile phase was a mixture of acetic acid/water/acetonitrile, 0.5:59.5:40. The flow rate was 1 mL min^{-1}.

several injections. In such a case, it is possible to electrochemically clean the electrode on-line by applying high positive potentials. To demonstrate this, we have carried out flow injection experiments with a high concentration (1 mM) of 1-naphthol in order to induce deactivation followed by electrochemical cleaning. Figure 7 shows the deactivation of the diamond electrode as
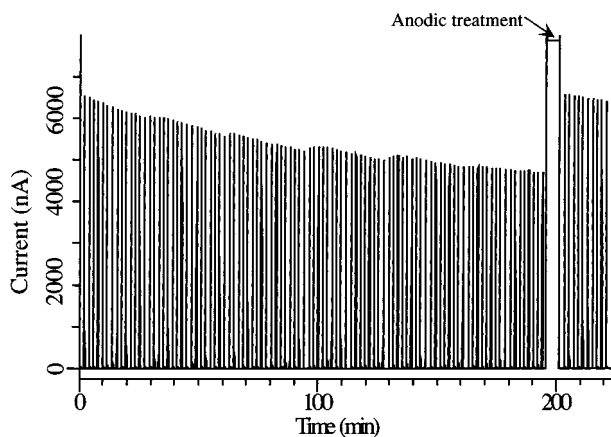
Figure 7. FIA-ED results for diamond electrode using 20-μL injections of 1 mM 1-naphthol. Applied potential, 0.8 V vs Ag/AgCl. The electrode was anodically treated at 3 V for 5 min after partial deactivation of the electrode. The mobile phase was a mixture of acetic acid/water/acetonitrile, 0.5:59.5:40. The flow rate was 1 mL min^{-1}.

Figure 8. Chromatograms for (A) 10 μM and (B) 10 nM standard prehydrolyzed carbamate pesticides. The applied potential at the diamond electrode was 0.9 V vs Ag/AgCl. The injection volume was 20 μL. The mobile phase was a mixture of acetic acid/water/acetonitrile, 0.5%:59.5%:40%. The flow rate was 1 mL min^{-1}.

evident from the 10% decrease in the current response after 100 injections. The electrode potential was then switched to +3.0 V, held for 30 min, and switched back to the detection potential of 0.9 V. A complete recovery of the current response was observed after this treatment and the background current remained the same. Comninellis and co-workers demonstrated the use of the diamond electrodes for wastewater treatment. The successful destruction of organics in wastewater was attributed to electro-generated oxidants/hydroxy radicals.[30,31] They showed the reactivation of the diamond electrode after fouling in 2-naphthol and 3-methylpyridine.[28,30] Thus, the diamond electrode also works as a dimensionally stable anode. This is another unique property of diamond, which makes it an interesting electrode.

Figure 8 shows the chromatograms obtained for high- and low-concentration mixtures of standard samples under optimized conditions. All three pesticides were eluted within 7 min, indicating rapid determination is possible. The most interesting observation is the high sensitivity of the diamond electrode, which allowed the well-defined chromatogram for a 10 nM (each) mixture of the analytes. This is specifically due to the low background noise of 10 pA, which is 50 times lower than the noise at 1.45 V used for direct detection. For the mixture containing each 10 nM concentration, we could observe an analytically useful signal for bendiocarb, while well-defined peaks were observed for carbofuran and carbaryl. The lowest detection limits at S/N = 2 is estimated to be 5 nM (1 ng/mL) for carbofuron, 3 nM (0.6 ng/mL) for carbaryl, and 10 nM (2 ng/mL) for bendiocarb. These limits are very close to the allowed levels of these pesticides. The calibration plots obtained for the three pesticides are very linear ($R = 0.999$) in the concentration range (10 nM–10 μM) studied (see Supporting Information).

CONCLUSIONS

Conductive boron-doped diamond electrodes have been shown to be very attractive for the detection of carbamate pesticides,
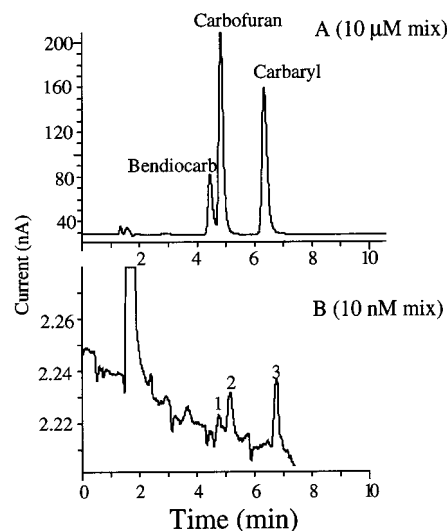
which exhibit high oxidation potentials (above 1.1 V vs SCE). The diamond electrodes are much superior to other carbon based-electrodes for the detection of underivatized carbamate pesticides, as they produce stable and sensitive response at high oxidation potentials. Even for detection at low operating potentials, as in the case of phenolic derivatives of carbamate pesticides, the diamond electrode exhibits excellent stability and sensitivity in comparison to GC. Our flow injection experiments show a current response variation of less than 2% for a 50 μM phenolic derivative of carbaryl. Additionally, we have also shown the complete recovery of current response after an on-line anodic treatment on fouled electrodes. This treatment is nearly independent of the nature of the adsorbed chemical species as the diamond electrode was proved to work like a dimensionally stable anode for waste treatment. The detection limits obtained for the three pesticides after the hydrolysis step are 5 nM (1 ppb) for carbofuron, 3 nM (0.6 ppb) for carbaryl, and 10 nM (2 ppb) for bendiocarb. These limits are well below the MRLs (1.2–1 ppm) for carbaryl, and carbofuran, and are in the same range reported by using well-established HPLC-fluorescence detection and ELISA methods. The present study demonstrates the potential utility of the diamond electrode for amperometric detection of carbamate pesticides.

SUPPORTING INFORMATION AVAILABLE

Calibration plots for underivatized and for prehydrolyzed carbamate pesticides. This material is available free of charge via the Internet at http://pubs.acs.org.

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