

Electrochemical Oxidation of Chlorophenols at a Boron-Doped Diamond Electrode and Their Determination by High-Performance Liquid Chromatography with Amperometric Detection

C. Terashima, Tata N. Rao, B. V. Sarada, D. A. Tryk, and A. Fujishima*

Department of Applied Chemistry, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Anodically pretreated diamond electrodes have been used for the detection of chlorophenols (CPs) in environmental water samples after high-performance liquid chromatographic (HPLC) separation. The anodization of as-deposited boron-doped polycrystalline diamond thin-film electrodes has enabled the stable determination of phenols over a wide concentration range. Prior to the HPLC analysis, a comparative study with ordinary glassy carbon, as-deposited diamond, and anodized diamond was made to examine the oxidative behavior of phenols by cyclic voltammetry and flow injection analysis with amperometric detection. At anodized diamond electrodes, reproducible, well-defined cyclic voltammograms were obtained even at high CP concentration (5 mM), due to a low proclivity for adsorption of the oxidation products on the surface. In addition, after prolonged use, the partially deactivated diamond could be reactivated on line by applying a highly anodic potential (2.64 V vs SCE) for 4 min, which enabled the destruction of the electrodeposited polymer deposits. Hydroxyl radicals produced by the high applied potential, in which oxygen evolution occurs, are believed to be responsible for the oxidation of the passivating layer on the surface. When coupled with flow injection analysis (FIA), anodized diamond exhibited excellent stability, with a response variability of 2.3% ($n = 100$), for the oxidation of a high concentration (5 mM) of chlorophenol. In contrast, glassy carbon exhibited a response variability of 39.1%. After 100 injections, the relative peak intensity, for diamond decreased by 10%, while a drastic decrease of 70% was observed for glassy carbon. The detection limit obtained in the FIA mode for 2,4-dichlorophenol was found to be 20 nM ($S/N = 3$), with a linear dynamic range up to 100 μ M. By coupling with the column-switching technique, which enabled on-line preconcentration (50 times), the detection limit was lowered to 0.4 nM ($S/N = 3$). By use of this technique, anodized diamond electrodes were demonstrated for the analysis of CPs in drainwater that was condensed from the flue gas of waste incinerators.

Phenols and substituted phenols such as chlorinated phenols (CPs) and related aromatic compounds are known to be common

components of industrial wastes. Another important mode of environmental contamination with CPs results from the fact that phenols react with chlorine during water treatment to produce CPs. Some of the larger and more common sources are pulp and paper mills,¹ petrochemical refineries,² plastics and glue manufacturers,³ coke plants, and leachate from municipal waste dumps.⁴ Various industrial effluents and municipal waste discharges typically contain CPs at concentrations from 1 to 21 mg L⁻¹.⁴ CPs in flue gases from waste incinerators are considered to be the precursors of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F).^{5–8} Most CPs are thought to be highly toxic and carcinogenic. In addition, several CPs are suspected to have activity as environmental endocrine disrupters. Since the pK_a 's of dichlorophenols range from 4.5 to 8.0, and the pH of natural waters can easily vary from 6.0 to 8.0, they are likely to be present mostly in the soluble ionic form in the environment. Therefore, CPs are considered to be priority pollutants by the U.S. Environmental Protection Agency (EPA).⁹

The detection of CPs in flue gas is of great environmental, industrial, and clinical significance. Although photochemical, chemical, and enzymatic methods have been developed, they are not very successful due to their complexity and their limitation to only a few CPs.¹⁰ Moreover, it is difficult to use gas chromatography/mass spectrometry (GC/MS) because the CPs have high solubility in water. A common type of sample is an aqueous solution, which is incompatible with GC/MS. Another approach for phenol detection, involves electrochemistry, e.g., voltammetry and amperometry, by which most phenols are oxidized at easily

- (1) Kristiansen, N.; Froshaug, M.; Aune, K.; Becher, G. *Environ. Sci. Technol.* **1994**, *28*, 1669–1973.
- (2) Rogers, K.; Gerlach, C. *Environ. Sci. Technol.* **1996**, *30*, 486A–491A.
- (3) Pavlov, B.; Terentyev, T. *Organic Chemistry*; Gordon and Breach Science Publishers: New York, 1965.
- (4) Gilman, A.; Douglas, U.; Arbuckle-Sholtz, T.; Jamieson, J. *Chlorophenols and Their Impurities: A Health Hazard Evaluation*; Bureau of Chemical Hazards, Environmental Health Directorate, National Health and Welfare: Ottawa, ON, Canada, 1982.
- (5) Ghorishi, S. B.; Altwicker, E. R. *Chemosphere* **1996**, *32*, 133–144.
- (6) Altwicker, E. R. *Chemosphere* **1996**, *33*, 1897–1904.
- (7) Weber, R.; Hagenmaier, H. *Chemosphere* **1999**, *38*, 529–549.
- (8) Hell, K.; Altwicker, E. R.; Stieglitz, L.; Addink, R. *Chemosphere* **2000**, *40*, 995–1001.
- (9) U.S. Environmental Protection Agency. Toxic Substance Control Act, 1979.
- (10) Durand, A.-P.; Brown, R. G.; Worrall, D.; Wilkinson, F. J. *Photochem. Photobiol. A: Chem.* **1996**, *96*, 35–43.

* Corresponding author: (tel.) 81 3 3812 2111, ext 9245; (fax) 81 3 3812 6227; (e-mail), akira-fu@fchem.chem.t.u-tokyo.ac.jp.

accessible potentials. These techniques, when coupled with separation techniques, can be highly sensitive. That is why the method of high-performance liquid chromatography (HPLC) with electrochemical detection has been applied in the analysis of CPs in various industrial-type wastewaters, including drainwater from municipal waste incinerators.

It is well known that the oxidation of phenolic compounds at solid electrodes produces phenoxy radicals, which couple to form a passivating polymeric film on the electrode surfaces.¹¹ The anodic reaction proceeds through an initial one-electron step to form phenoxy radicals, which subsequently can undergo either polymerization or further oxidation with transfer of oxygen from hydroxyl radicals at the electrode surface to produce *o*-benzoquinone and *p*-benzoquinone.¹¹ As a consequence of radical formation with subsequent polymerization, the practical oxidative destruction of phenols has become problematic due to the inevitable fouling of the anode surface. Surface fouling, due to the building of adsorbed reaction products, also causes problems in the electroanalysis of phenols. The electrochemically generated passive film is strongly adherent and continuous over 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 slurried 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.¹² The optimum parameters for the electrochemical treatments of glassy carbon, however, are dependent on the electroactive reactants. In the case of the electrochemical treatment of wastewater, PbO₂ anodes were investigated to minimize electrode corrosion during the oxidation of organic compounds, including phenols.^{13,14} Kawagoe and Johnson demonstrated the utility of bismuth-doped lead dioxide electrodes (Bi-PbO₂), which exhibit relatively low overpotentials for anodic O₂ evolution and thus facilitate the mechanical removal of the passivating layer by means of bubble evolution between the films and substrates.¹⁵ Modification of electrodes with an electroactive polymer layer prior to their use in electroanalysis is another approach to stabilize the electrode response for the detection of phenols. Although such modified electrodes exhibited improved performance in the detection of phenols by HPLC-ECD, they could not be reactivated on-line.^{16–18} For practical applications, the methods used for reactivation of the electrodes should be simple, rapid, and reproducible.

It is worthwhile to search for a new electrode material that could overcome the above problems to some extent. Highly boron-doped diamond electrodes, which have recently emerged, appear to be promising in this regard. These have recently received a great deal of attention,¹⁹ particularly for electroanalysis, owing to their unique electrochemical properties: e.g., (i) wide electro-

chemical potential window in aqueous solutions,²⁰ (ii) very low background current,²¹ and (iii) long-term stability of the response.^{22,23} Anodically pretreated diamond electrodes have recently been shown to be useful for the selective detection of dopamine and uric acid in the presence of ascorbic acid.^{23,24} These electrodes have also exhibited excellent stability and high reproducibility. Also, diamond, like other dimensionally stable oxide electrodes (e.g., PbO₂, SnO₂, and Ru-TiO₂),²⁵ has a high overpotential for oxygen production. The diamond electrode is reported to be promising for the treatment of phenols in wastewater.^{26,27} In the potential region of water discharge on diamond, highly oxidizing hydroxyl radicals were proposed to be produced, which cause the complete oxidation of organic compounds in solution, as well as passive organic films.^{28,29}

In the present work, we used anodically oxidized diamond electrodes for the electrochemical oxidation of CPs by cyclic voltammetry, hydrodynamic voltammetry, and flow injection analysis (FIA) in the amperometric mode. Similar experiments were conducted at as-deposited diamond electrodes and glassy carbon electrodes, for comparison. The results illustrate that anodized diamond electrode exhibits excellent resistance to fouling even in the presence of high concentrations of CPs. This outstanding performance is assumed to be due to the anodically generated oxygen functional groups that repel phenoxy radicals, which are responsible for the formation of polymeric films. Finally, we demonstrated the application of this electrode for the simple, versatile, and accurate HPLC-amperometric detection of 11 CPs in the drainwater condensed from the flue gas of waste incinerators.

EXPERIMENTAL SECTION

Highly boron-doped diamond electrodes were deposited on Si-(100) wafers using a high-pressure microwave plasma-assisted chemical vapor deposition (CVD) system (ASTeX Corp., Woburn, MA). The details of the preparation have been described previously.²¹ A mixture of acetone and methanol in the ratio of 9/1 (v/v) was used as the carbon source. B₂O₃, the boron source, was dissolved in the acetone-methanol solution at a B/C weight ratio of 10⁴ ppm. High-purity hydrogen was used as the carrier gas. The bubbling of the acetone-methanol-B₂O₃ solution was carried out at ~25 °C. The deposition of the film was carried out at a microwave power of 5 kW. A film thickness of ~40 μm was

(11) Gattrell, M.; Kirk, D. W. *J. Electrochem. Soc.* **1993**, *140*, 903–911.

(12) Wang, J.; Lin, M. S. *Anal. Chem.* **1988**, *60*, 499–502.

(13) DeScure, V.; Watkinson, A. *Can. J. Chem. Eng.* **1981**, *59*, 852.

(14) Fleszar, B.; Ploszynska, J. *Electrochim. Acta* **1985**, *30*, 31–42.

(15) Kawagoe, K. T.; Johnson, D. C. *J. Electrochem. Soc.* **1994**, *141*, 3404–3409.

(16) Wang, J.; Li, R. *Anal. Chem.* **1989**, *61*, 2809–2811.

(17) Dall'Orto, V. C.; Danilowicz, C.; Sobral, S.; Balbo, A. L.; Rezzano, I. *Anal. Chim. Acta* **1996**, *336*, 195–199.

(18) Mafatle, T.; Nyokong, T. *Anal. Chim. Acta* **1997**, *354*, 307–314.

(19) Rao, T. N.; Fujishima, A. *Diamond Relat. Mater.* **2000**, *9* (3–6), 384–389.

(20) Strojek, J. W.; Granger, M. C.; Dallas, T.; Holtz, M. W.; Swain, G. M. *Anal. Chem.* **1996**, *68*, 2031–2037.

(21) Yano, T.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *J. Electrochem. Soc.* **1998**, *145*, 1870–1876.

(22) Rao, T. N.; Yagi, I.; Miwa, T.; Tryk, D. A.; Fujishima, A. *Anal. Chem.* **1999**, *71*, 2506–2511.

(23) Popa, E.; Notsu, H.; Miwa, T.; Tryk, D. A.; Fujishima, A. *Electrochem. Solid-State Lett.* **1999**, *2* (1), 49–51.

(24) Popa, E.; Kubota, Y.; Tryk, D. A.; Fujishima, A. *Anal. Chem.* **2000**, *72*, 1724–1727.

(25) Rodgers, J. D.; Jedral, W.; Bunce, N. J. *Environ. Sci. Technol.* **1999**, *33*, 1453–1457.

(26) Fryda, M.; Herrmann, D.; Schafer, L.; Klages, C.; Perret, A.; Haenni, W.; Comninellis, C.; Gandini, D. *New Diamond Front. Carbon Technol.* **1999**, *9* (3), 229–240.

(27) Hagans, P. L.; Natishan, P. M.; Stoner, B. R.; O'Grady, W. E. *J. Electrochem. Soc.* **2001**, *148*, E298–E301.

(28) Panizza, M.; Duo, I.; Michaud, P. A.; Cerisola, G.; Comninellis, C. *Electrochem. Solid-State Lett.* **2000**, *3* (9), 429–430.

(29) Foti, G.; Gandini, D.; Comninellis, C.; Perret, A.; Haenni, W. *Electrochem. Solid-State Lett.* **1999**, *2* (5), 228–230.

achieved after 10 h of deposition. The film resistivity, measured by the four-point probe method, was on the order of $10^{-3} \Omega \text{ cm}$. The film quality was confirmed by Raman spectroscopy (Renishaw System 2000). The Raman spectra of diamond films showed them to be of high quality, as evident from the strong characteristic peak at 1332 cm^{-1} . In addition, a broad peak centered at $\sim 1200 \text{ cm}^{-1}$ was observed, which is characteristic of highly boron-doped samples. No additional peaks due to sp^2 carbon are observed around 1500 cm^{-1} , indicating the high quality of these films.

Electrochemical measurements were made with a potentiostat/galvanostat (Hokuto Denko Research, model HZ-3000). Cyclic voltammograms were obtained at a scan rate of 0.1 V s^{-1} . The electrochemical studies were performed in a single-compartment glass cell. The planar working electrode was mounted on the bottom of the glass cell by use of a silicon O-ring. The geometric area of the electrode in the cell was estimated to be 0.09 cm^2 . A commercial saturated calomel electrode (SCE) was used as the reference, and a Pt coil was used as the counter electrode. All measurements were made at room temperature ($23 \pm 2^\circ \text{C}$). The electrolyte was a Britton–Robinson buffer solution (pH 2.0), composed of a mixture of boric, acetic, and phosphoric acids (each 0.04 M) and adjusted to the appropriate pH by the addition of 0.2 M NaOH .³⁰ The solutions were deoxygenated with nitrogen for 10 min prior to analysis. The glassy carbon electrode (Tokai Carbon Co., Ltd.) was pretreated by polishing with diamond paste, followed by ultrasonication in high-purity water before the experiment. Anodic pretreatment of the diamond electrode was carried out by passing a charge of $\sim 720 \text{ mC cm}^{-2}$ at an applied potential of $+ 2.64 \text{ V}$ versus SCE for 4 min, in pH 2 Britton–Robinson buffer. The XPS results obtained before and after anodization for the as-deposited diamond revealed that the surface O/C ratio increased from 0.02 to 0.15 (see Supporting Information). These O/C ratios are in agreement with our previous report on oxidized diamond that was treated in 0.1 M KOH .³¹

The FIA system used in the present study consisted of a binary pump (GL Sciences, Inc., PU611), an autosampler (Spark-Holland, Triathlon) for constant $10\text{-}\mu\text{L}$ injections, a thin-layer flow cell (GL Sciences, Inc.), an amperometric detector (Bioanalytical Systems, LC-4C), and a data acquisition system (EZChrom Elite, Scientific Software, Inc.). The wall-jet-type flow cell consisted of the Ag/AgCl reference electrode and a stainless steel (type 316) counter electrode. A $200\text{-}\mu\text{m}$ -thick Teflon gasket was used as a spacer in the cell. The geometric area of the electrode in the cell was estimated to be 0.4 cm^2 . During experiments, the flow cell was kept at $25 \pm 0.1^\circ \text{C}$. The mobile phase for FIA consisted of 60% methanol–water containing 0.5% phosphoric acid, and the flow rate was set at 0.2 mL min^{-1} in order to match the HPLC conditions.

The HPLC analysis was performed with the column-switching technique, which involved two columns, a short cleanup column ($50 \text{ mm} \times 2.1 \text{ mm i.d.}$) and an analytical column ($150 \text{ mm} \times 2.1 \text{ mm i.d.}$), which were connected to a six-port valve. Weakly polar compounds and ions such as Cl^- and Br^- contained in the samples injected are eluted from a cleanup column prior to the elution of the polar target CPs. Then, the automatic six-port valve is

programmed to switch to allow a fraction of the sample to flow into an analytical column to perform the sample separation. The valve is again switched back after all of the target compounds containing di- and tri-CPs are eluted, to avoid the flow of strong polar compounds remaining on the short column into the analytical column. GL Sciences, Inc., supplied the chromatographic column (Inertsil ODS-3). The HPLC system was equipped with an electrochemical detector (ED623, GL Sciences, Inc.) in which we could use both diamond and glassy carbon electrodes. The flow cell and HPLC columns were thermostated to 35°C . The optimum working electrode potential for the measurement of CPs was 1.2 V versus Ag/AgCl. The sample injection volumes were 10 and $500 \mu\text{L}$ in the FIA and HPLC analyses, respectively.

RESULTS AND DISCUSSION

Cyclic Voltammetry. The oxidation of phenol was examined at as-deposited (AD) diamond and anodically oxidized (AO) diamond before the electrochemical oxidation of the CPs. Figure 1 (parts A and B) shows the assignment of the products during phenol oxidation at AD and AO diamond, respectively. It is known that the main products in phenol oxidation are *o*-benzoquinone (*o*-BQ) and *p*-benzoquinone (*p*-BQ).¹¹ Both AD and AO diamond electrodes yielded a single anodic peak in the first cycle of the cyclic voltammogram corresponding to phenol oxidation. The products of *o*-BQ and *p*-BQ were confirmed by comparing the voltammograms obtained for authentic compounds in the presence and the absence of phenol (Figure 1).

In the case of 2,4-dichlorophenol (2,4-DCP), which was taken as a representative of CP, the cyclic voltammetric oxidation peak potential was found to be 0.95 V versus SCE (Figure 2), which is less positive than that of phenol (see Figure 1A). This trend is in agreement with that obtained for the glassy carbon (GC) electrode, which was in contrast to the expectation because chlorinated phenols are more resistant to oxidation.²⁵ The reason for this behavior is explained in a later section. Table 1 summarizes the results of the anodic peak potentials for phenol, 2,4-DCP, hydroquinone, and catechol. At AO diamond, the peak potential was shifted to 1.37 V . After the first cycle, new peaks appeared for both electrodes, as in the case of phenol. Although, according to Polcaro and Palmas,³² chlorinated benzoquinone is assumed to be the main oxidation product, it is to be confirmed experimentally. The variation of the potential sweep rate (v) for both kinds of diamond electrodes showed that the peak currents for 0.1 mM 2,4-DCP are linearly proportional to $v^{1/2}$, within the range $0.005\text{--}0.5 \text{ V s}^{-1}$ indicating that the oxidation current is diffusion controlled.

The voltammogram for phenols at carbon electrodes is known to exhibit a linear dependence of the anodic peak potential on pH, with a slope of 58 mV/pH under pH 10.³³ We have examined the pH dependence for 2,4-DCP oxidation at diamond electrodes. It is known that the $\text{p}K_a$ of the phenol decreases as the number of chlorine atoms substituted on the ring increases. Figure 3 shows the pH dependence of peak potential for 0.1 mM 2,4-DCP at AD and AO diamond. The E_p versus pH plots in both cases are linear below pH 8, the value being in good agreement with the $\text{p}K_a$ of 2,4-DCP.³⁴ Below pH 8, the slope of the E_p versus pH plots

(30) Dobos, D. *Electrochemical Data: A Handbook for Electrochemists in Industry and Universities*; Akademiai Kiado: Budapest, 1975; p 239.

(31) Notsu, H.; Yagi, I.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *Electrochem. Solid State Lett.* **1999**, *2* (10), 522–524.

(32) Polcaro, A. M.; Palmas, S. *Ind. Eng. Chem. Res.* **1997**, *36*, 1791–1798.

(33) Bub, V. F. P.; Wisser, K.; Lorenz, W. J.; Heimann, W. *Ber. Bunsen-Ges. Phys. Chem.* **1973**, *77*, 823–828.

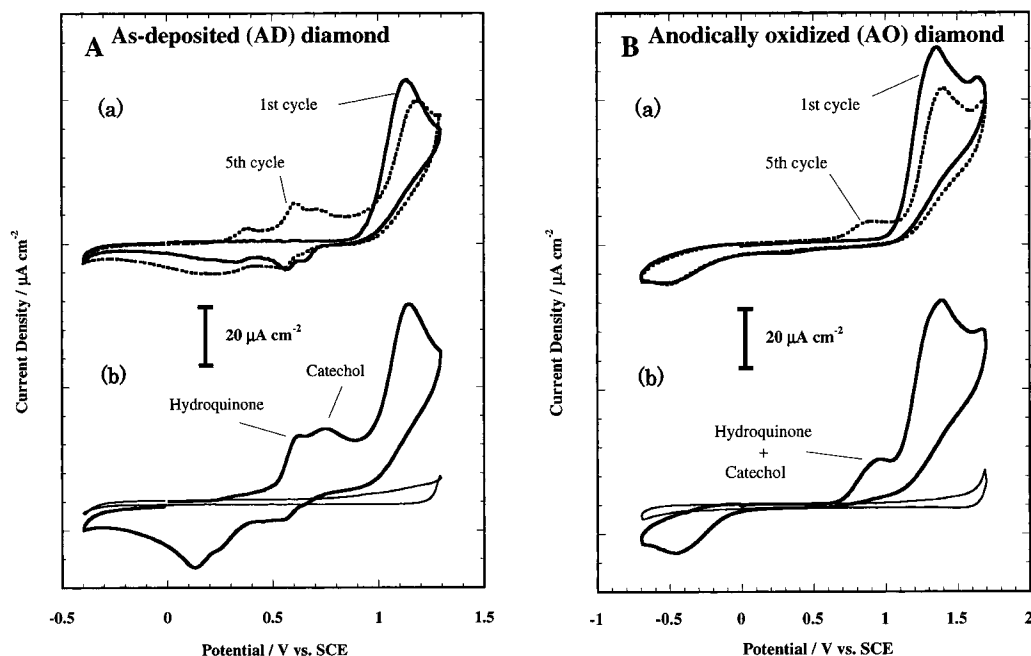


Figure 1. Cyclic voltammograms for 0.1 mM phenol in Britton–Robinson buffer (pH, 2) at (A) AD diamond and (B) AO diamond (a) in the absence and (b) in the presence of catechol and hydroquinone (0.02 mM each). Thin lines in (b) show the residual voltammograms. The potential sweep rate was 0.1 V s^{-1} .

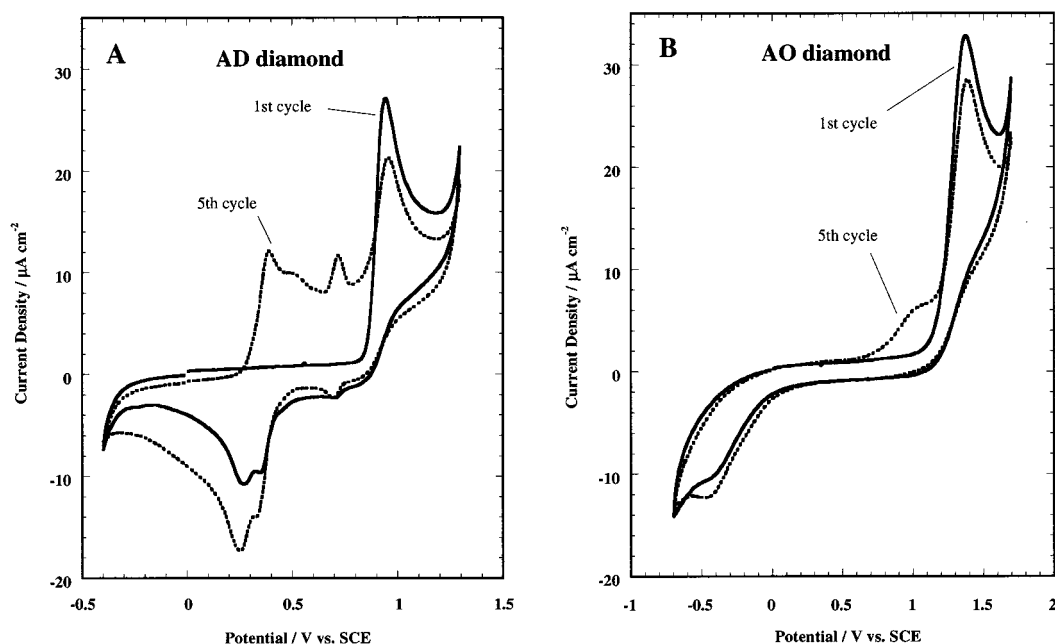


Figure 2. Cyclic voltammograms for 0.1 mM 2,4-dichlorophenol in Britton–Robinson buffer (pH, 2) at (A) AD diamond and (B) AO diamond electrodes. The potential sweep rate was 0.1 V s^{-1} .

at AD and AO diamond were estimated to be 66 and 87 mV/pH, respectively. The slope at AD diamond is reasonably close to 59 mV/pH, indicating the participation of equal numbers of protons and electrons in the oxidation reaction. A possible reason for the higher slope (87 mV/pH) at AO diamond could be associated with the higher positive potential required for phenol oxidation at AO diamond, because in this potential range, it is likely that the hydroxyl radicals produced may involve other side reactions. Furthermore, the inflection point of the E_p versus pH plots in

Figure 3 correlates well with the pK_a value of 2,4-DCP (7.85).³⁴ Above this pH, all of the compound is in the phenolate form, which is oxidized more easily than the neutral phenol.

Phenols can be used as model compounds to examine electrode stability because of their well-known electrode-fouling properties. Unmodified GC electrodes undergo rapid deactivation during the oxidation of phenols.¹⁶ To be successful in the electroanalysis of phenols at the diamond electrode, we must ensure its stability by examination of repetitive measurements. We have first examined the durability of diamond electrodes at high 2,4-DCP concentration, because it was observed previously

(34) Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1993; Vol. 6, p 156.

Table 1. Peak Potentials of Phenol, 2,4-Dichlorophenol, Hydroquinone, and Catechol in Britton–Robinson Buffer (pH 2.0)^a

electrode	E _p ^{ox} (V vs SCE)			
	phenol ^b	2,4-dichlorophenol ^b	hydroquinone ^b	catechol ^b
as-deposited (AD) diamond	1.13	0.95	0.66	0.78
anodically oxidized (AO) diamond	1.37	1.37	0.90	0.95

^a Potential sweep rate, 0.1 V s⁻¹. ^b Concentration, 0.1 mM.

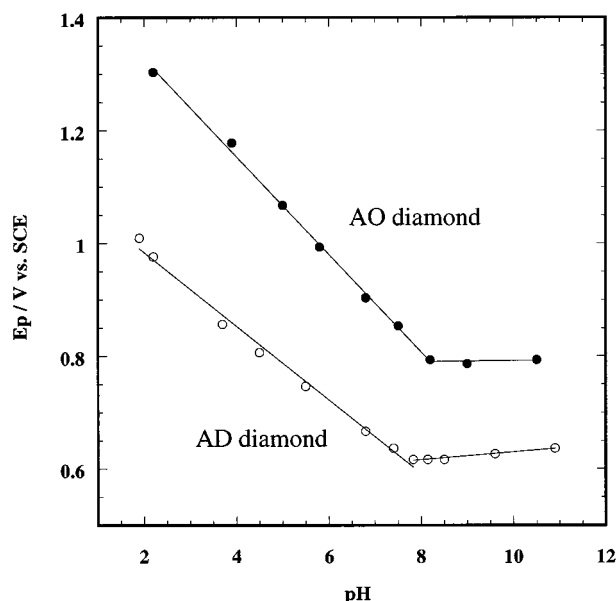


Figure 3. pH dependence of the peak potential for 0.1 mM 2,4-dichlorophenol at AD and AO diamond electrodes in Britton–Robinson buffer.

that the fouling of the electrode is pronounced at higher concentrations.¹⁶ Figure 4A compares the first cycle and the fifth cycle of cyclic voltammograms for 5 mM 2,4-DCP at an AD diamond electrode. A GC electrode was also examined for comparison. The peak potentials for 2,4-DCP were ~1 V versus SCE at both electrodes, with the peak current for AD diamond being twice that of GC. For both the electrodes, the peak current disappeared by the fifth cycle due to electrode fouling. In this state, no recovery of the peak current could be accomplished after a few minutes of recovery time, even after vigorous stirring. A possible reason for the lower peak current at the GC electrode is that at high phenol concentration the fouling of GC becomes more rapid and the current does not reach its peak value due to rapid coverage of the passive layer due to slow adsorption of oxidation products at electrode surface. At lower concentration (e.g., 0.3 mM), we observed nearly the same peak current for GC and diamond in the first cycle. At the diamond electrode, as reported by other workers,³⁵ polar molecules, such as anthraquinonedisulfonate, do not adsorb, while they remain strongly adsorbed on the surfaces of GC that contain polar oxygen functionalities.

Interestingly, however, the peak current recovers when the fouled AD diamond electrode is anodically treated in the solution at 2.64 V versus SCE for 4 min (Figure 4A b). At high anodic

potentials, diamond is expected to produce hydroxyl radicals, which can completely oxidize the passive layer on the diamond film.²⁹ Panizza et al. demonstrated the effect of such treatment to recover the activity of diamond in the detection of 2-naphthol.²⁸ The treatment potential 2.64 V versus SCE is in the water discharge region for the diamond electrode but, according to Panizza et al., also involves the production of hydroxyl radicals. Another observation in this study is that the voltammetric peak potential has shifted dramatically to a more positive potential, moving from 1.0 to 1.4 V due to anodic oxidation. No further shift in the peak potential was observed after repeated treatments. The observed anodic shift of the voltammetric peak is probably because the surface dipoles on the oxidized diamond electrostatically repel both anions and neutral molecules.^{31,36} Recently, our group experimentally confirmed the presence of C=O and OH groups on the oxidized polycrystalline diamond surface by the surface modification of DNPH and APTES, respectively.^{37,38} Martin and Morrison also demonstrated the presence of OH functional groups on the diamond surface after anodic polarization, while they could not see the C=O feature, which may be hidden underneath the H₂O vapor bands.³⁹ The possibility of diamond surface oxide dipoles was further tested with other redox analytes that are positively charged (Fe³⁺/Fe²⁺), negatively charged (Fe(CN)₆⁴⁻/Fe(CN)₆³⁻), and uncharged (ascorbic acid in acidic pH). The results obtained with these species are well in agreement with our previous reports^{31,36–38} and other reports⁴⁰ related to ion–dipole and dipole–dipole interactions. It is very interesting and surprising that the AO diamond electrodes appear to be less prone to fouling than AD diamond electrodes, as is evident from the well-defined voltammogram obtained in the fifth cycle (Figure 4A). Gattrell and Kirk concluded that phenoxy radicals play an important role in producing these types of passive films on the electrode surface.^{41,42} We believe that the type of functional groups and their distribution over the surface are the factors that control the adsorption behavior of oxidized diamond. Although polar molecules are expected to adsorb on an oxygen-covered surface containing polar oxygen functional groups, the situation in the case of diamond seems to be different. We believe that oxygen groups such as carbonyl or hydroxyl groups formed on the

(36) Yagi, I.; Notsu, H.; Kondo, T.; Tryk, D. A.; Fujishima, A. *J. Electroanal. Chem.* **1999**, 473, 173–178.

(37) Notsu, H.; Yagi, I.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *J. Electroanal. Chem.* **2000**, 492, 31–37.

(38) Notsu, H.; Fukazawa, T.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *Electrochem. Solid-State Lett.* **2001**, 4 (3), H1–H3.

(39) Martin, H. B.; Morrison, P. W. *Electrochem. Solid-State Lett.* **2001**, 4 (4), E17–HE20.

(40) Granger, M. C.; Swain, G. M. *J. Electrochem. Soc.* **1999**, 146, 4551–4558.

(41) Gattrell, M.; Kirk, D. W. *J. Electrochem. Soc.* **1992**, 139, 2736–2744.

(42) Gattrell, M.; Kirk, D. W. *J. Electrochem. Soc.* **1993**, 140, 1534–1540.

(35) Xu, J.; Chen, Q.; Swain, G. M. *Anal. Chem.* **1998**, 70, 3146–3154.

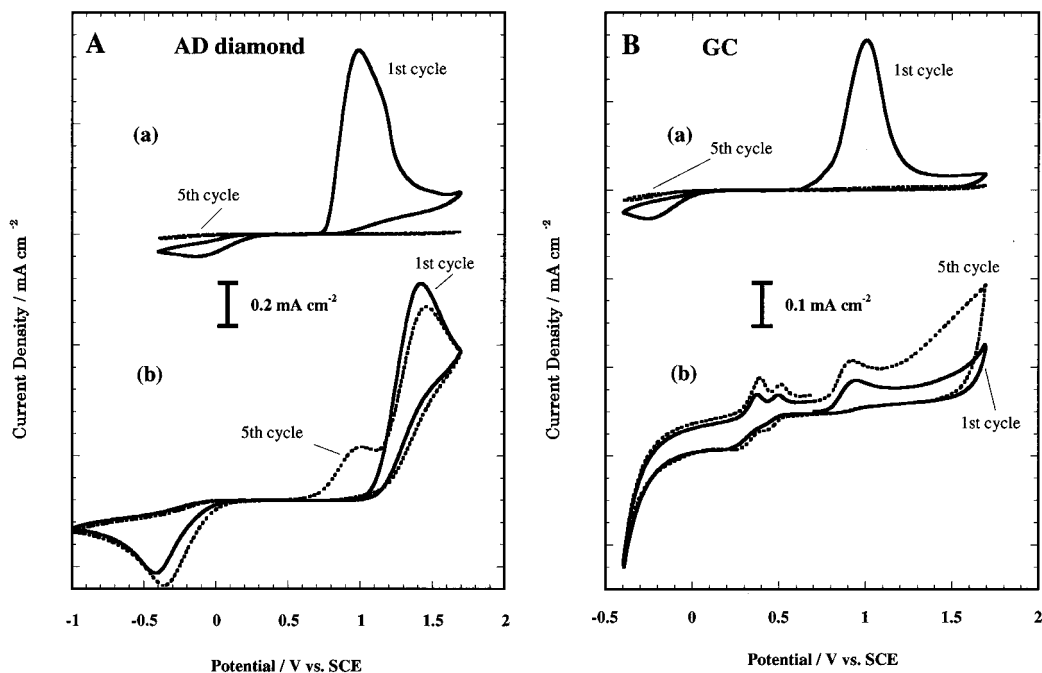


Figure 4. Cyclic voltammograms for a high-concentration (5 mM) 2,4-dichlorophenol in Britton–Robinson buffer (pH, 2) at (A) AD diamond and (B) GC electrodes. (a) At the AD electrodes, due to the high concentration, electrode fouling was observed after the fifth cycle. (b) After fouling was observed, both electrodes were subjected to electrochemical treatment at 2.64 V for 4 min in order to examine the possibility of reactivation.

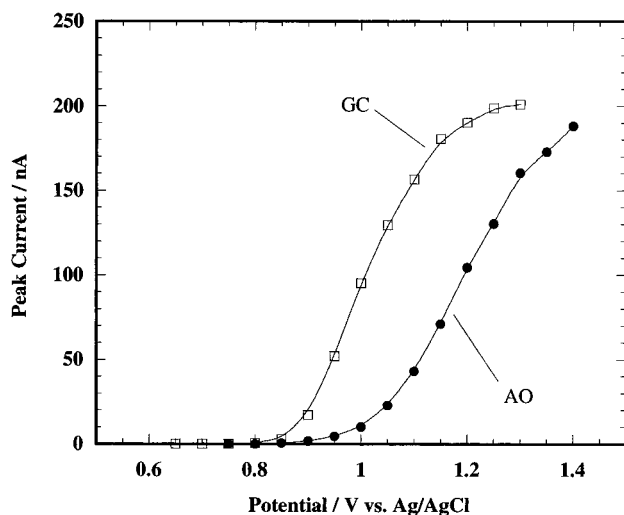


Figure 5. Hydrodynamic voltammograms for 6.2 μM 2,4-dichlorophenol at AO diamond and GC electrodes. The injection volume was 10 μL . The mobile phase was 60% methanol containing 0.5% phosphoric acid. The flow rate was 0.2 mL min^{-1} .

diamond surface are well aligned on the facets of microcrystals, which are expected to form a negative surface dipolar field. This field probably repels the phenols or their reaction products, resulting in very low adsorption and an anodic shift in the peak potential. In contrast, the anodic oxidation of GC using the same conditions has resulted in only slight recovery of the peak current but a drastic increase in the background current due to surface oxidation and increase in surface area (Figure 4B b). The first cycle of the cyclic voltammogram after the anodization of the damaged GC showed two anodic peaks, at 0.4 and 0.5 V. These two peaks correspond to the oxidation of hydroquinone and catechol. It is expected that these compounds are incorporated into the passive film.

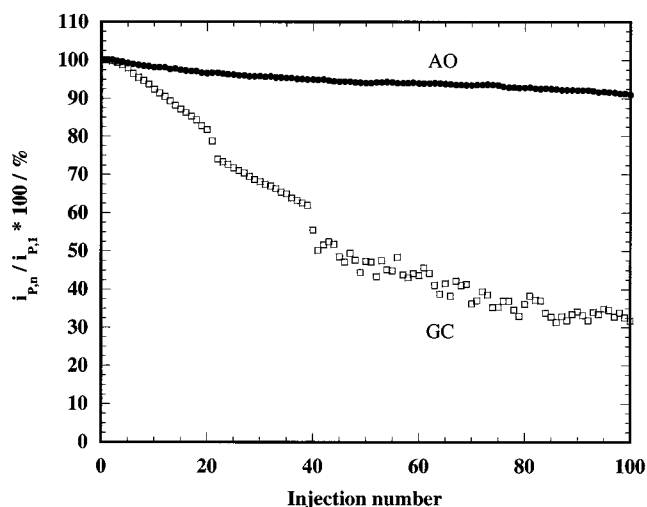


Figure 6. Differential response of FIA peak heights for high-concentration 2,4-dichlorophenol at AO diamond and GC. The mobile phase was 60% methanol–water containing 0.5% phosphoric acid at a 0.2 mL min^{-1} flow rate; 10 μL of 5 mM 2,4-dichlorophenol was successively injected.

Flow Injection and HPLC Analysis. Figure 5 shows a hydrodynamic voltammogram for 6.2 μM 2,4-DCP at GC and AO diamond. The mobile phase was 60% methanol–water containing 0.5% phosphoric acid. Although high methanol content has slightly increased the polymerization reaction, our results indicated that this mobile phase is very suitable for the separation of the 11 CPs examined. The half-wave potentials of the hydrodynamic i – E curves are found to be more positive than the E_p of the cyclic voltammogram obtained in the same mobile phase, as well as in Britton–Robinson buffer (pH 2.0). This may be because of low conductivity of the mobile phase in the thin-layer flow cell. The half-wave potential (1.2 V vs Ag/AgCl) for AO diamond is 0.2 V

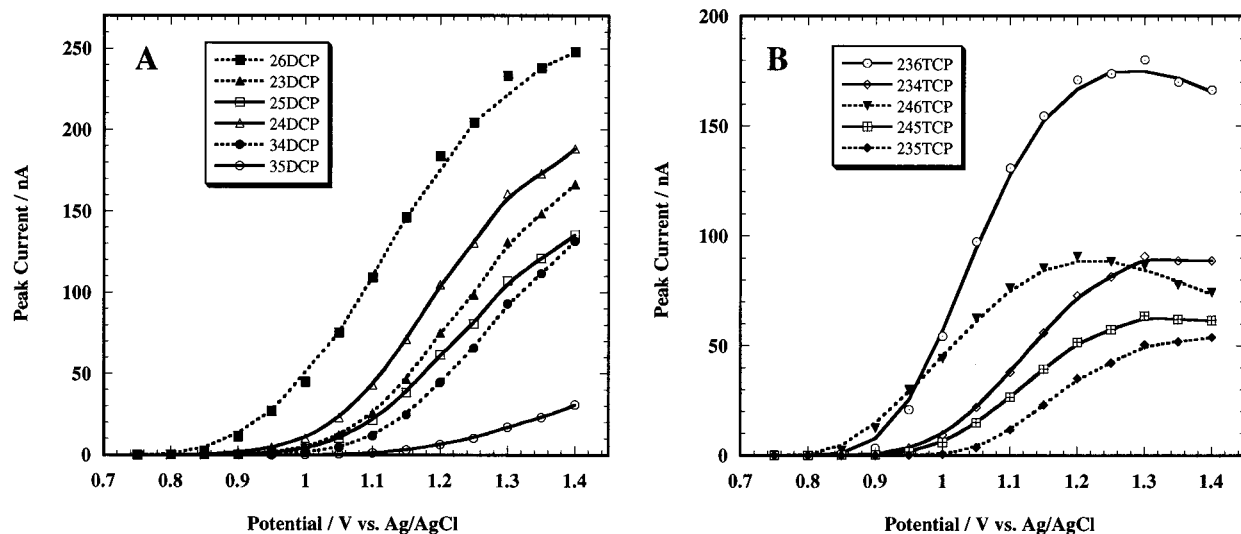


Figure 7. Hydrodynamic voltammograms for (A) dichlorophenols ($6.2 \mu\text{M}$ each) and (B) trichlorophenols ($5.1 \mu\text{M}$ each) at AO diamond. Other conditions were the same as in Figure 5.

more positive than that for the GC electrode (1.0 V vs Ag/AgCl).

Figure 6 illustrates the FIA results for 100 repetitive injections of 5 mM 2,4-DCP at GC and AO diamond electrodes. The detection potential was 1.2 V for GC and 1.4 V for the AO diamond. A highly stable detection peak is observed when AO diamond is used with a relative standard deviation (RSD) of 2.3% and with a decrement of $\sim 10\%$ in the relative peak intensity (Figure 6). As mentioned above, phenol oxidation produces polymer film on the electrode. In the FIA, since hydrodynamic mass transport is caused by the solution flowing through a cell, the mobile phase carries electrogenerated product away from the electrode surface, depending on the flow rate.⁴³ This phenomenon helps in minimizing the deactivation of the electrode in FIA compared to a bulk-solution experiment such as cyclic voltammetry. Nevertheless, repetitive injections of highly concentrated 2,4-DCP at GC resulted in a 70% reduction of the peak height. The value of RSD in the peak height ranges from 30 to 40%. After this durability experiment, a visible passivating layer could be observed on the GC surface. Under flow conditions, fouling of the electrode is not rapid but there is a gradual deactivation due to continuous deposition of polymer on the GC electrode surface.

During the FIA measurements, we also examined the reactivation of the electrode in situ by applying a high positive potential (2.64 V vs SCE). The AO diamond electrodes could be readily recovered by pretreatment after 100 injections (not shown). It is pertinent to note that the background current of the AO diamond stabilizes quickly within 10 min after switching to the operating potential, while GC required 60 min to stabilize, at a substantially higher background value. These results are in agreement with those reported using AD diamond.^{44,45} An experimental detection limit of 20 nM , with a linear dynamic range from 20 nM to $100 \mu\text{M}$ ($r = 0.9996$), was achieved in the FIA mode. Thus, AO diamond electrodes show excellent response reproducibility and

rapid stabilization of the background current and are expected to be promising electrode materials for the practical application of the electrochemical detection of phenols.

Figure 7 depicts hydrodynamic voltammetric i - E curves for several CPs at AO diamond for the HPLC conditions used in the present work. The flow rate of the mobile phase was 0.2 mL min^{-1} , which was optimized according to the microbore separation column. Well-defined sigmoidal curves are seen for all dichlorophenols (DCPs) (Figure 7A) and trichlorophenols (TCPs) (Figure 7B). A general observation is that TCPs appear to oxidize at lower potentials than the DCPs, which is in contrast to expectation, because the higher chlorinated phenols are more difficult to undergo oxidation. However, this apparent discrepancy is due to the fact that the current for the TCP falls at a relatively negative potential without attaining a limiting value, due to the formation of an insoluble deposit on the electrode surface.²⁵ It is also important to note that the current for 2,6-DCP, for example, is higher than that of 2,3,6-TCP due to the same reason. The hydrodynamic voltammograms shown in Figure 7 also indicate that the meta-chlorinated phenol, for example, 3,5-DCP, is more difficult to oxidize than the ortho-chlorinated 2,6-DCP. The potential for amperometric detection was set at 1.2 V vs Ag/AgCl , where all CPs produce significant currents, and to avoid interference from other impurities in real samples. The column-switching technique, which has been applied in many applications to environmental and biological monitoring,⁴⁶ was used for the present analysis. This technique is very attractive for sample cleanup and routine analysis, which allows the analysis to be completed in a shorter time. Also, for analyses that require ultrahigh sensitivity, large-volume injection of purely aqueous samples adjusted to low pH were adopted in reversed-phase partition chromatography in order to achieve an effective preconcentration effect. A typical chromatogram of a standard sample mixture containing each CP at the 1 ng mL^{-1} (ppb) level is shown in Figure 8A. This chromatogram was automatically obtained by use of the column-switching technique. The detection limits were

(43) Alden, J. A.; Compton, R. G. *Anal. Chem.* **2000**, *72*, 199A–203A.

(44) Sarada, B. V.; Rao, T. N.; Tryk, D. A.; Fujishima, A. *Anal. Chem.* **2000**, *72*, 1632–1638.

(45) Rao, T. N.; Sarada, B. V.; Tryk, D. A.; Fujishima, A. *J. Electroanal. Chem.* **2000**, *491*, 175–181.

(46) Nielsen, S. E.; Freese, R.; Cornett, C.; Dragsted, L. O. *Anal. Chem.* **2000**, *72*, 1503–1509.

Table 2. Limits for Chlorophenols Estimated from Figure 8A and the Concentrations Detected in Figure 8B

Compound	LOD ^a (ng mL ⁻¹)	detected conc (ng mL ⁻¹)	compound	LOD ^a (ng mL ⁻¹)	detected conc (ng mL ⁻¹)
2,6-DCP	0.038	14.8	2,3,6-TCP	0.059	27.0
2,3-DCP	0.082	39.6	2,3,4-TCP	0.072	76.7
2,5-DCP	0.076	26.9	2,4,6-TCP	0.098	34.4
2,4-DCP	0.065	27.9	2,4,5-TCP	0.102	85.1
3,4-DCP	0.073	23.6	2,3,5-TCP	0.092	61.6
3,5-DCP	0.361	9.1			

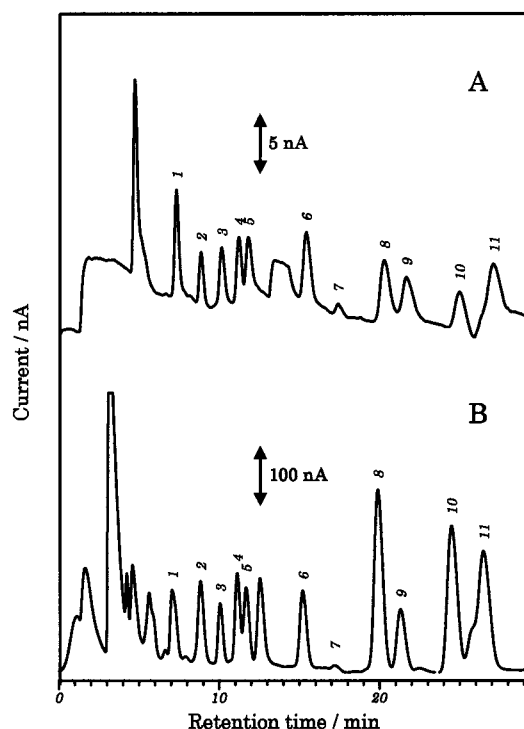
^a S/N = 3.

Figure 8. Typical chromatograms for (A) standard chlorophenols (1 ng mL⁻¹ each) and (B) a real sample (drainwater from a waste incinerator) without any pretreatment. The drainwater from the waste incinerator was directly injected to the column-switching HPLC. The applied potential at the AO diamond electrode was 1.2 V vs Ag/AgCl. The injection volume was 500 μ L. The peak assignments are (1) 2,6-DCP, (2) 2,3-DCP, (3) 2,5-DCP, (4) 2,4-DCP, (5) 3,4-DCP, (6) 2,3,6-TCP, (7) 3,5-DCP, (8) 2,3,4-TCP, (9) 2,4,6-TCP, (10) 2,4,5-TCP, and (11) 2,3,5-TCP.

estimated to be in the range of 0.038 ng mL⁻¹ (0.23 nM) for 2,6-DCP to 0.361 ng mL⁻¹ (2.23 nM) for 3,5-DCP (S/N = 3). In addition, Figure 8B shows a chromatogram for a drainwater sample from a municipal waste incinerator. The quantification of the substances was carried out by comparison of the chromatograms for samples versus standard mixtures, and additionally, the identification was confirmed by LC/MS/MS measurements.⁴⁷ The detected concentrations of CPs in the drainwater sample are presented in Table 2.

CONCLUSIONS

Anodically pretreated (AO) boron-doped diamond thin-film electrodes have been shown to be best suited for the electro-

chemical detection of CPs. Anodic pretreatment of diamond is crucial to achieve high stability and reproducibility of the electrode performance. Another advantage of AO diamond is that the electrochemical reactivation of diamond is also possible by applying a high positive potential (2.64 V vs SCE). In this way, complete recovery of the current response is possible, due presumably to the destruction of the passive film by electrogenerated hydroxyl radicals. Such a treatment is not effective for glassy carbon, for which the treatment resulted in substantial increases in the background current. The outstanding stability of AO diamond electrodes was demonstrated by coupling with an FIA system, where the response variability for a concentrated (5 mM) 2,4-DCP solution was only 2.3% after 100 injections. An experimental detection limit of 20 nM, with a linear dynamic range from 20 nM to 100 μ M ($r = 0.9996$), was achieved in the FIA mode. When coupled with chromatography, the sample volume injected was very large owing to the reversed-phase column-switching technique, so that the detection limit was further lowered to 0.4 nM due to an on-line preconcentration factor of 50. Using HPLC with the column-switching technique and coupling with the diamond electrode detector, we were able to detect 11 CPs (Table 2) in water samples obtained from a municipal incineration plant. AO diamond has great potential as an electrode for the detection of phenols in water samples from a wide range of sources.

ACKNOWLEDGMENTS

This research was supported by the Japan Society for the Promotion of Science (JSPS), Research for the Future Program, "Exploratory Research on Novel Artificial Materials and Substances for Next Generation Industries". The authors gratefully acknowledge technical assistance from Mr. K. Yamasaki, Mr. M. Furuno (GL Sciences, Inc.), and Dr. I. Watanabe (National Institute of Public Health) with the real sample measurements of CPs.

SUPPORTING INFORMATION AVAILABLE

Survey X-ray photoelectron spectra for AD diamond and AO diamond. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Received for review June 19, 2001. Accepted November 27, 2001.

AC010681W

(47) Watanabe, I.; Terashima, C.; Yamasaki, K.; Ikeguchi, T., manuscript in preparation.