Use of a Bentonite-modified Carbon Paste Electrode for the Determination of Some Phenols in a Flow System by Differential-pulse Voltammetry

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The electrochemical behaviour of some phenols (methyl-, chloro- and nitrophenols) included in the US Environmental Protection Agency List of Priority Pollutants at a bentonite-modified carbon paste electrode in a flow system was studied. A fixed proportion of artificial sea-water was used in the sample solution so that the applicability of the methodology to marine environments could be tested. Amounts of bentonite from 5 to 10% were used. For methyl- and nitrophenols, a good stability of the electrode surface activity was observed after a series of repeated injections, with relative standard deviations between 0.40 and 2.98% ($n = 16$). Recovery studies were carried out on real sea-water samples spiked with 0.5 or 2.5 mg l^{-1} of the pollutants; recoveries from 95.4 to 101.1% were obtained.

Keywords: *Bentonite-modified carbon paste electrode; differential-pulse voltammetry; phenol derivatives; flow injection analysis*

The contaminants that enter water through human activities, such as detergents, plasticizers, pesticides, products of water chlorination and industrial wastes, are of great interest to water analysis programmes. Hundreds of such compounds have been identified, and more than 100 have been designated Priority Pollutants by the US Environmental Protection Agency (EPA).[1]

Phenols are well suited to electrochemical detection since they can be oxidized at a solid electrode. Chlorophenols find many applications in insecticides, fungicides, antiseptics and disinfectants. The utility of electrochemical detection for measurement of chlorinated as well as non-chlorinated phenols was demonstrated by Armentrout *et al.*,[2] and HPLC with electrochemical detection has been used for the determination of phenol and phenolic compounds,[2] as well as cyclic voltammetry at a carbon paste electrode in flowing liquids.[3] Electrochemical detection of 2-nitrophenol and other nitrophenols at a mercury electrode by scanning voltammetry in HPLC has been described.[4,5] The differential-pulse technique has been used in stripping voltammetry at a mercury electrode in a flow injection system.[6,7]

Carbon paste electrodes have a wide range of anodic and cathodic utility and are inexpensive and easy to prepare and replace. These electrodes also have several drawbacks, such as a high cathodic residual current, a low resistance towards mechanical damage and electrochemical polymerization of analytes.[8,9] To retain their advantages and remove most of the drawbacks, modified carbon paste electrodes incorporating exchanger resins and clays have been studied. The bentonites exhibit similar properties to other clays. These materials are able to adsorb an electroactive species for its direct determination.[10–14] Bentonite is an impure montmorillonite with adsorbent properties.[15] Several groups have reported the use of clay film electrodes.[16,17] Electrode surfaces modified with clay offer the advantages of high chemical stability, known structural features and low cost. The electrochemistry of clay-modified electrodes is a subject of considerable interest;[18] recently, clay-modified electrodes have been used for studying transport in layered materials.[19]

In this paper, a bentonite-modified carbon paste electrode was used for the determination of some pollutants included in the US EPA List of Priority Pollutants (methyl-, chloro- and nitrophenols) by differential-pulse voltammetry in a flow system.

Experimental

Apparatus

The flow injection system consisted of a Gilson (Villiers-le-Bel, France) Minipuls-2 peristaltic pump and a Rheodyne (Cotati, CA, USA) 5020 sample injection valve with variable injection volumes. The electrochemical cell was a Metrohm (Herisau, Switzerland) 656 electrochemical detector equipped with a carbon paste working electrode, a silver–silver chloride reference electrode and a gold auxiliary electrode. The flow cell was connected to a Metrohm 611 detector coupled to a Metrohm 612 scanner; this electrochemical device carried out the scanning voltammetric measurements. The injection system was connected to the flow cell through 0.5 mm id Teflon tubing. The signals were registered on a Hewlett-Packard (Avondale, PA, USA) Model 862/D x–y recorder.

Reagents and Materials

The modified carbon pastes were prepared by mixing 5 g of graphite (spectroscopic grade) with 1.8 ml of mineral oil and the necessary amount of modifier to obtain the required mass proportion. The resulting paste was packed into the electrode making direct contact with the platinum wire at the bottom of the cavity, and the surface was smoothed.

Oxygen was removed from analysis solutions by purging with nitrogen.

Artificial sea-water was prepared by dissolving different salts in 1 l of doubly distilled water [10 g of $MgCl_2$, 1.5 g of $CaCl_2$, 0.7 g of KCl, 4 g of Na_2SO_4 and 23 g of NaCl, all from Merck (Darmstadt, Germany), analytical-reagent grade]. A formic acid–sodium formate or a Britton–Robinson buffer solution was used as carrier solution.

Pollutant stock solutions [5000 mg l^{-1}, from Merck, Riedel-de Häen (Hannover, Germany) and Supelco (Bellefonte, PA, USA), analytical-reagent grade] were prepared in ethanol (Merck, analytical-reagent grade); working solutions were prepared daily by diluting with doubly distilled water.

Spectroscopic graphite was obtained from Ringsdorff-Werke, (Bonn, Germany), mineral oil from Sigma (St. Louis, MO, USA) and bentonite and zeolite from Aldrich (Milwaukee, WI, USA).

Procedures

The buffer solution was used as carrier. An artificial sea-water–buffer solution (1 + 4) with a pollutant concentration of 5 mg l^{-1} was used as sample. After purging with nitrogen (if necessary), a sample volume of 0.25 ml was injected into the carrier stream at a flow rate of 1.25 ml min^{-1} and the measurements were carried out by the differential-pulse technique at the carbon paste modified electrode. A pulse amplitude of ±100 mV was used for all the experiments.

Amounts of bentonite from 5 to 10% were used. High percentages of bentonite produce an increase in the residual current and in the peak width, and give a less compact paste that could separate from the electrode as a result of the flow.

For pentachlorophenol, a formic acid–sodium formate buffer solution of pH 4 was used. Bentonite was used to modify the carbon paste at a level of 7.5%. The same buffer solution but of pH 5 was used for 4-chloro-3-methylphenol, and the measurements were carried out at a modified carbon paste electrode containing 10% bentonite.

The detection of 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol and 2,4-dimethylphenol was studied using a Britton–Robinson buffer solution of pH 4 and a modified carbon paste electrode containing 5% bentonite.

The data were recorded by various types of plot. Conventional *i–E* recordings were obtained for stopped-flow voltammograms. When the flow injection system was used, *i–t* plots were recorded.

For the stopped-flow voltammograms, a volume of 0.25 ml of the sample (pollutant concentration 5 mg l^{-1}) was injected into the carrier stream. The flow was stopped when the maximum of the flow peak reached the detector, and the voltammogram was registered.

For the electrode study, scans were performed continuously. Repeated injections were carried out without removing the paste from the electrode, in order to verify the maintenance of the electrode surface in a reproducible, active state. The injection frequency depended on the peak width.

Recovery studies of some phenols were carried out on different spiked sea-water samples; these samples were taken in the Bay of Cádiz.

Results and Discussion

Stopped-flow Voltammograms

The stopped-flow voltammograms of the pollutants are shown in Figs. 1 and 2. Dimethyl- and chlorophenols are oxidized at a carbon paste electrode whereas polynitrophenols are electroreducible species.

Dimethyl- and chlorophenols show a peak potential in the anodic range; a well defined single peak is obtained for each compound. For polynitrophenols, cathodic peak potentials are obtained and the same rapid scan technique was applied. These compounds produce two peaks, the first being sharper and higher than the second. The peak potentials for the two peaks are very close, and there is a strong overlap of the signals; greater overlapping is obtained for 2,4-dinitrophenol than for 2-methyl-4,6-dinitrophenol.

In order to obtain the optimum *i–t* plots, the influence of scan rate and potential range was studied for each pollutant. Since fast scans were carried out continuously, each *i–t* peak was composed of as many scans as could be performed during the passage of the sample through the detector. Because the scans were performed continuously, it could be ensured that several scans had been run at the maximum of the flow peak (the measurement interval was sufficiently short). For example, the voltammetric variables for 2,4-dinitrophenol were a scan rate of 100 mV s^{-1} and a potential range from −450 to −475 mV; the extrapolated peak width was about 20 s. Under these conditions, four complete scans can be made every second (0.25 s per scan) and 80 scans can be run during the passage of the sample through the detector. Fig. 3 shows the *i–t* plots for pentachlorophenol and 2,4-dinitrophenol when the potential range or the scan rate is modified within an appropriate range.

Both chlorophenols showed oxidation potentials within the accessible anodic range for the carbon electrode. For pentachlorophenol, the scans were performed between 850 and 925 mV, and a scan rate of 1 V s^{-1} was used. The same scan rate was chosen as the optimum value for 4-chloro-3-methylphenol, and a potential range of 750–800 mV was used. For polynitrophenols, a scan rate of 100 mV s^{-1} was used. The potential range studied was around the peak potential of the first peak. Within this potential zone the background noise is smaller and the difference between the peak current of the pollutant and the

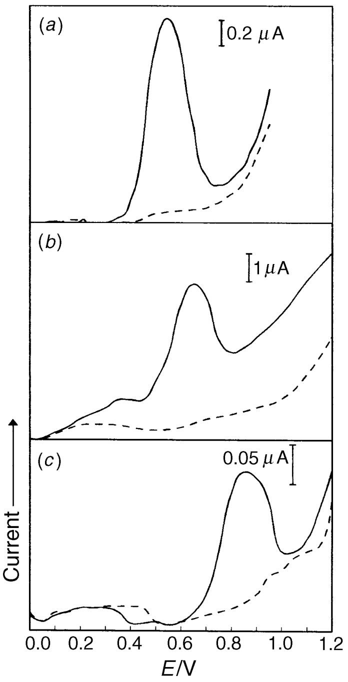

Fig. 1 Stopped-flow voltammograms for (*a*) 4-chloro-3-methylphenol, (*b*) 2,4-dimethylphenol and (*c*) pentachlorophenol. Pollutant concentration, 5 mg l^{-1}; pulse amplitude, 100 mV; scan rate, (*a*) and (*b*) 100 mV s^{-1} and (*c*) 50 mV s^{-1}. Background currents (---) are also shown.

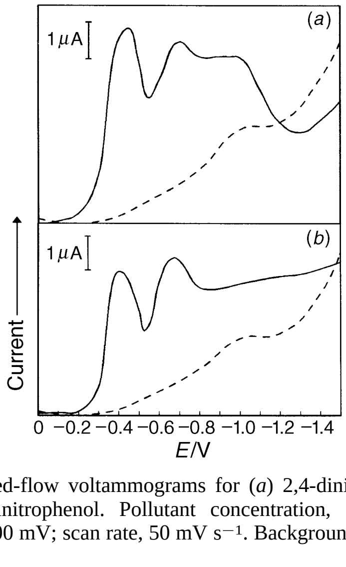

Fig. 2 Stopped-flow voltammograms for (*a*) 2,4-dinitrophenol and (*b*) 2-methyl-4,6-dinitrophenol. Pollutant concentration, 5 mg l^{-1}; pulse amplitude, −100 mV; scan rate, 50 mV s^{-1}. Background currents (---) are also shown.

background current is higher than for the second peak. Similar potential ranges were chosen for polynitrophenols: from −450 to −475 mV for 2,4-dinitrophenol, and from −400 to −425 mV for 2-methyl-4,6-dinitrophenol.

The single anodic peak obtained for 2,4-dimethylphenol was also studied by differential-pulse voltammetry. The *i*–*t* plots were recorded at a scan rate of 100 mV s^{-1}; a potential range of 650–700 mV was used for subsequent studies.

Stability of the Electrode Surface

Problems connected with the stability and reproducibility of the electrode are often substantially less serious in flow measurements than in batch experiments, as the electrode is continuously washed by the carrier liquid and is only exposed to relatively short analyte zones.

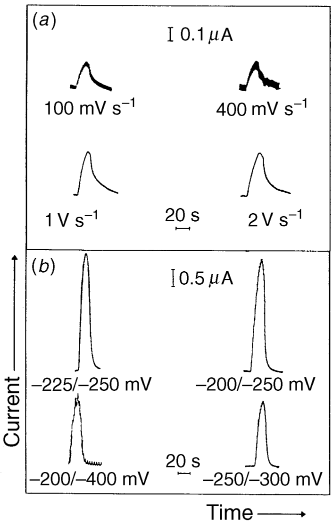

Fig. 3 (*a*) Influence of scan rate on *i*–*t* peaks for pentachlorophenol. Potential range, 850–925 mV; flow rate, 1.25 ml min^{-1}; volume injected, 0.25 ml. (*b*) Influence of potential range on *i*–*t* peaks for 2,4-dinitrophenol. Scan rate, 100 mV s^{-1}; flow rate, 1.25 ml min^{-1}; volume injected, 0.25 ml.

The use of a carbon paste electrode in the detector cell and its application to a flow injection system require that the surface activity of the working electrode should be constant, at least during the time of a single complete analysis. For each pollutant, repeated injections were carried out without removing the modified carbon paste from the electrode. The injection frequency depended on the peak width of each analyte. The peak height and the relative standard deviation are shown in Table 1.

A good stability of the electrode surface was observed for 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol and 2,4-dimethylphenol. After a series of repeated injections, the peak intensity remained virtually constant during the time of the analysis; it is not necessary to remove the paste from the electrode after each new injection. Thus, under these experimental conditions, the determination of 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol and 2,4-dimethylphenol could be carried out at a bentonite-modified carbon paste electrode in a flow injection system.

For pentachlorophenol and 4-chloro-3-methylphenol, peak height decreased after each new injection under the experimental conditions described previously. The repeated injections were stopped when a significant decrease in intensity was observed. In conventional electrochemical experiments with phenols, insoluble polymeric products can be formed which adhere to the electrode surface, diminishing the rate of the electron transfer step. This leads to a decrease in the efficiency of the electrode in oxidizing the phenol, and this is observed as a decrease in current response.[20] This fact made it difficult to establish conditions for the electrochemical determination of pentachlorophenol and 4-chloro-3-methylphenol in a flow injection system.

In view of the good characteristics of the *i*–*t* peak for 4-chloro-3-methylphenol (high intensity, well-defined and sharp-edged peak), several changes to the analytical conditions were made in an attempt to improve the stability of the electrode surface. Different modifiers in the carbon paste (5 and 10% bentonite and 5% zeolite) and different buffer solutions of pH 5

Table 1 Influence of repeated injections on the stability of the electrode surface. The values of the *i*–*t* peaks (μA) are shown

	4-Chloro-3-methylphenol							
	Bentonite*							
Injection No.	10%	5%	Zeolite* 5%	Bentonite† 10%	Pentachloro-phenol‡	2-Methyl-4,6-dinitrophenol§	2,4-Dinitro-phenol§	2,4-Dimethyl-phenol§
1	3.26	2.83	3.20	0.45	0.42	2.80	4.16	2.52
2	3.04	2.54	2.80	0.44	0.37	2.85	4.16	2.52
3	3.02	2.30	2.49	0.43	0.36	2.90	4.16	2.60
4	2.65	—	—	0.42	0.34	2.92	4.17	2.60
5	2.49	—	—	0.42	0.33	2.92	4.17	2.60
6	2.35	—	—	0.41	0.30	2.95	4.16	2.61
7	2.19	—	—	0.41	0.29	3.01	4.18	2.61
8	2.04	—	—	0.40	0.29	3.01	4.16	2.60
9	1.96	—	—	0.40	0.28	3.01	4.17	2.62
10	—	—	—	0.38	—	3.01	4.18	2.62
11	—	—	—	—	—	3.05	4.18	2.62
12	—	—	—	—	—	3.07	4.20	2.62
13	—	—	—	—	—	3.08	4.20	2.62
14	—	—	—	—	—	3.08	4.20	2.62
15	—	—	—	—	—	3.08	4.20	2.62
16	—	—	—	—	—	3.08	4.20	—
RSD (%)	18.33	10.38	12.57	5.26	14.04	2.98	0.40	1.29

* Concentration, 5 mg l^{-1}; acetic acid–sodium acetate buffer solution of pH 5. † Concentration, 0.5 mg l^{-1}; formic acid–sodium formate buffer solution of pH 5. ‡ Carbon paste electrode containing 10% bentonite; formic acid–sodium formate buffer solution of pH 4; concentration, 5 mg l^{-1}. § Carbon paste electrode containing 5% bentonite; Britton–Robinson buffer solution of pH 4; concentration, 5 mg l^{-1}.

(acetic acid–sodium acetate and formic acid–sodium formate) were tested. A more dilute sample solution with an analyte concentration of 0.5 mg l^{-1} was also tested. No improvement of the electrode was obtained under the new experimental conditions tested. Only the use of a more dilute sample solution led to better results, but the variation of the peak height was still excessive.

Application to Real Sea-water Samples

To validate the results obtained for 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol and 2,4-dimethylphenol, recovery studies were carried out on different spiked sea-water samples. The samples injected contained either 0.5 or 2.5 mg l^{-1} of the pollutants. The determinations carried out for each pollutant gave recoveries between 95.4 and 101.1% for a 0.5 mg l^{-1} concentration (relative standard deviation 1.0–5.0%), and between 98.4 and 99.2% for a 2.5 mg l^{-1} concentration (relative standard deviation 1.1–3.4%).

In conclusion, the use of a bentonite-modified carbon paste electrode allows the electrochemical detection of several phenols in a flow injection system. A good electroanalytical behaviour is obtained for all the pollutants tested, but the peak height for chlorophenols decreases after each new injection. The electrode surface activity is constant for the other phenols; for these compounds, recovery studies were carried out on real sea-water samples spiked with different pollutant concentrations, and good results were obtained. The modified carbon paste electrode described is inexpensive and easy to prepare and replace, and it can be used for both reduction and oxidation reactions.

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