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Voltammetric Determination of 2-Nitrophenol at a Bentonite-Modified Carbon Paste Electrode

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Abstract. A bentonite-modified carbon paste electrode has been applied to the determination of 2-nitrophenol by differential pulse voltammmetry. The electrochemical reduction of 2-nitrophenol at -0.8 V is carried out in an artificial sea water-formic acid/sodium formate medium at pH 4. The peak height was found to be dependent on the pH over the range 2–11; the presence of a secondary process was observed in the pH range 8–11. The peak potential showed a dependence on pH, with two linear regions with different slopes. A linear relationship between peak intensity and concentration was obtained in the range 0.07–10 $\mathrm{mg\,l^{-1}}$, with a detection limit of 0.03 $\mathrm{mg\,l^{-1}}$ and a coefficient of variation of 1.3% at 5 $\mathrm{mg\,l^{-1}}$. The effects of organic and inorganic species on the 2-nitrophenol determination were studied with a view to testing the resolution of the voltammetric technique. The proposed method has been applied to sea water samples with good results.

Key words: bentonite-modified carbon paste electrode, differential pulse voltammetry, 2-nitrophenol.

Phenols have received considerable attention in waste water analysis programs, and a wide variety of analytical techniques for their determination has been reported. 2-Nitrophenol is one of the nitrophenols included in the U.S. Environmental Protection Agency List of Priority Pollutants [1, 2]; its presence in the environment is currently a matter of concern because of its toxicity.

Several chromatographic techniques have been applied to the determination of nitrophenols, such as liquid chromatography with ultraviolet detection and gas chromatography with mass spectrometry or flame ionization detection [3–5]. Good detection limits can be achieved from direct injection of the water sample if fluorescence or electrochemical detection is used [6].

Liquid chromatography has been applied to the determination of nitrophenols with different electroanalytical detectors: a mercury electrode [7] and fast-scan electrochemical detectors [8, 9]. The use of different electroanalytical techniques has been also described: polarography, a.c. polarography, cyclic voltammetry and adsorptive stripping voltammetry [10–13]. The use of C_{18} in a carbon paste electrode for the determination of nitrophenols has been recently reported [14].

Voltammetric methods are particularly suited to the analysis of a wide variety of organic compounds. Carbon paste electrodes are superior to the other solid electrodes in having a lower residual current and noise, and in being very cheap and easy to prepare and replace. To retain the advantages of carbon paste electrodes and remove most of their drawbacks, modified carbon paste electrodes have been studied, with incorporation of exchanger resins and clays [15–19]. The bentonites exhibit similar properties to those of other clays; the zeolites have also been used as modifiers for carbon pastes. These materials are able to adsorb electroactive species for their direct determination. In this paper, the electrochemical reduction of 2-nitrophenol at a bentonite-modified carbon paste electrode is studied, and a method for the direct voltam-

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metric determination of the pollutant in sea water is proposed. The modified carbon paste electrode could also be used as electrochemical detector for HPLC, so improving substantially the selectivity of the determinations, as has been described for a wide variety of compounds [20].

Experimental

Apparatus

A Metrohm E-506 Polarecord coupled to a 663 VA stand was used for voltammetric experiments, with a rotating carbon paste working electrode (surface area 7 mm^2), an Ag/AgCl/3 *M* KCl reference electrode and a platinum auxiliary electrode.

Reagents and Materials

The bentonite-modified carbon paste was prepared by mixing 5 g of graphite (spectroscopic grade) with 1.8 ml of mineral oil and the necessary amount of bentonite to obtain the required mass proportion. The resulting paste was packed into the electrode and the surface was smoothed. After each measurment the paste was removed and the cavity of the electrode was cleaned and dried.

Artificial sea water was prepared by dissolving different salts in 11 of twice-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, analytical reagent grade). Different pH values were obtained by addition of 1 *M* NaOH to a Britton-Robinson buffer solution. A formic acid/sodium formate buffer solution of pH 4 and ionic strength 0.05 was used to fix the optimum value of pH.

2-Nitrophenol stock solutions (5000 mg l^{-1}, Fluka, analytical reagent grade) were prepared in ethanol (Merck, analytical reagent grade); working solutions were prepared daily by dilution with ethanol.

Spectroscopic graphite was obtained from Ringsdorff-Werke GMBH, Bonn, Germany; mineral oil from Sigma and bentonite from Aldrich.

Procedures

Voltammetric procedure for the study of variables: 40 ml of artificial sea water and 10 ml of buffer solution were placed in the electrochemical cell. After purging with nitrogen for 15 min, a voltammogram was recorded by differential pulse voltammetry with a scan rate of 20 mV s^{-1} and a potential range from 0 to -2 V. After addition of 50 µl of the 2-nitrophenol solution a new voltammogram was recorded. The paste was then removed from the electrode; the cleaning and packing procedures were repeated before new measurements.

For the preliminary studies, a Britton-Robinson buffer solution of pH 4 was used. These experiments were performed in stirred 5 mg l^{-1} 2-nitrophenol solutions, with a pulse amplitude of -80 mV and a rotation rate of 1500 rev min^{-1}. For the accumulation studies, the bentonite-modified carbon paste electrode was placed in the cell containing the stirred 2-nitrophenol solution and the circuit remained open.

Calibration graph preparation and study of interferences were carried out in the operating conditions obtained through the study of variables: a 5% bentonite-modified carbon paste electrode, a scan rate of 20 mV s^{-1}, a pulse amplitude of -100 mV and a rotation rate of 3000 rev min^{-1}.

Determination of 2-nitrophenol in spiked sea water: A volume of 40 ml of sea water sample spiked with 2-nitrophenol solution and 10 ml of formic acid/sodium formate buffer solution of pH 4 and ionic strength 0.05 was used as sample. The determination was carried out in the operating conditions described for calibration graph and study of interferences. The standard addition method was used for the determination.

Results and Discussion

Preliminary Studies

When a bentonite-modified carbon paste electrode was used, an increase in peak height was observed over that obtained at an unmodified electrode: for 5 mg l^{-1} 2-nitrophenol, the peak height was 100 times higher than that obtained at an unmodified electrode. A smaller increase was obtained when a zeolite-modified electrode was used.

The influence of the accumulation time at a 5% bentonite-modified electrode was studied; this parameter could influence the degree of adsorption of 2-nitrophenol at the electrode. Figure 1 shows a typical accumulation curve; it can be observed that the peak height did not increase significantly with accumulation time. As the presence of bentonite increases the peak height, a role of adsorption must be suggested. If the influence of accumulation time is negligible, then the adsorption is fast and the process is not controlled by adsorption. Only a few values of the potential of accumulation could be investigated because our instrumentation only allowed potentials to be set with a variation of 0.2 V (0, -0.2, -0.4, etc.). For these values, no significant influence on peak height was observed.

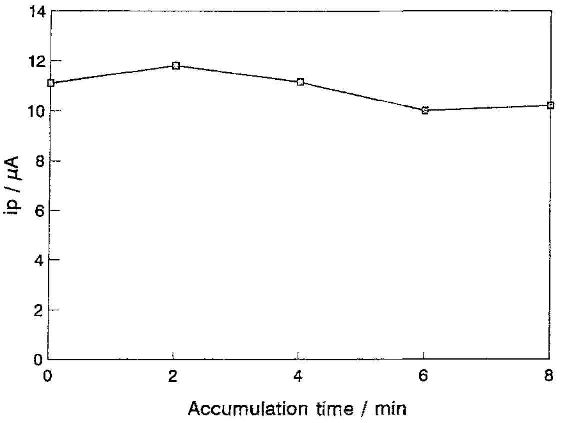

Fig. 1. Effect of accumulation time on peak height for a 5 mg l^{-1} 2-nitrophenol solution at a 5% bentonite-modified carbon paste electrode. Pulse amplitude -80 mV, scan rate 20 mV s^{-1}, rotation rate 1500 rev min^{-1}

Influence of pH

Studies on the effect of pH were carried out at a 2-nitrophenol concentration of 5 mg l^{-1} at pH 2–11 with a Britton-Robinson buffer solution. The peak potential, E_p, shows a dependence on pH, with two linear regions with different slopes, and an intersection point at pH 7.15, which agrees with the pK_a value reported in the literature [21]. The presence of a secondary process was observed in the pH range 8–11; the E_p for this process was independent of pH. At pH 11, only the secondary process occurred. The main process is probably due to reduction of the nitro group to an amino group. Several products can be obtained from reduction of the nitro group in basic media [22]. The peak height, i_p, reaches its maximum value in acidic media. Figure 2 shows the influence of pH on E_p and i_p. Well-defined peaks were obtained for 2-nitrophenol in the pH range 2–6. The i_p decrease with increasing pH; two peaks were observed in the pH range 8–10; at pH 11 the signal for the main process disappears. Different voltammograms in the pH range 2–9 can be observed in Fig. 3. The optimum pH for further studies was pH 4.

Influence of Buffer Solution

Artificial sea water: buffer solution (4:1) with several buffer solutions of pH 4 and at different ionic strength (I) were studied to find the effect on the analyte determination.

The results are shown in Table 1. There are significant differences in i_p; different peak heights are observed for a given buffer due to effect of ionic strength.

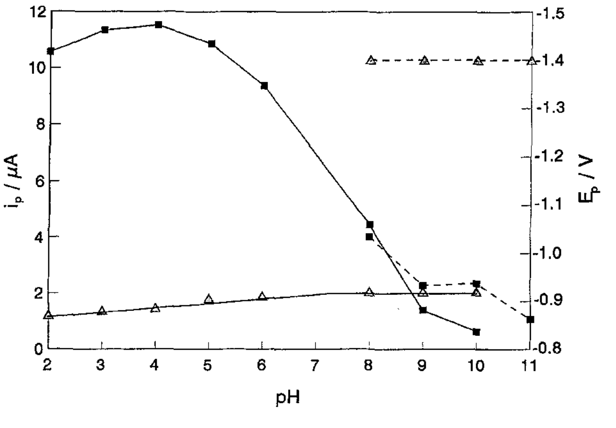

Fig. 2. Effect of pH on E_p (▲) and i_p (■) for the main (———) and secondary (----) process, for a 5 mg l^{-1} 2-nitrophenol concentration at a 5% bentonite-modified carbon paste electrode. Pulse amplitude −80 mV, scan rate 20 mV s^{-1}, rotation rate 1500 rev min^{-1}

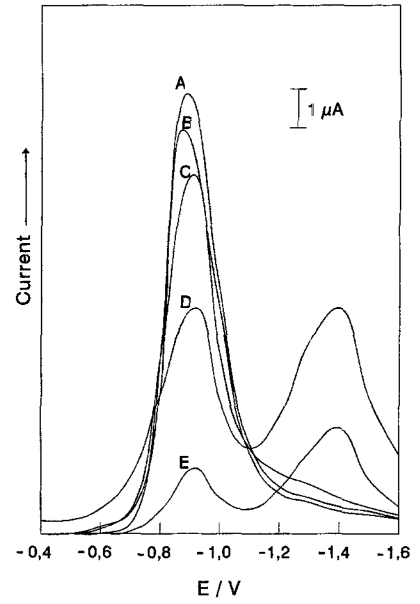

Fig. 3. Voltammograms of 2-nitrophenol (5 mg l^{-1}) for different pH values: A4, B2, C6, D8, and E9

Table 1. Influence of buffer solution and ionic strength

Buffer solution (pH 4)	i_p(µA)	E_p(V)
Acetic acid/sodium acetate, $I = 0.05$	7.8	−0.85
Acetic acid/sodium acetate, $I = 0.1$	10.2	−0.85
Formic acid/sodium formate, $I = 0.05$	12.2	−0.80
Formic acid/sodium formate, $I = 0.1$	10.3	−0.80
Britton-Robinson	10.5	−0.88

E_p is different with each buffer solution although there is no influence of ionic strength for a given buffer. The best results are obtained with the formic acid/sodium formate buffer soution with a ionic strength of 0.05 and pH 4; in this case an i_p maximum is obtained and also a less negative E_p.

Effect of Percentage of Bentonite

The behaviour of the electrode is improved when bentonite is used in the preparation of the carbon paste. The proportion of bentonite mixed with the carbon paste is a control factor of great interest.

As expected, an increase in the percentage gives a higher i_p, at least up to 15–20% bentonite, but at the same time an increase in the residual current is produced due to the higher impedance of the electrode; the peak width also increased with the percentage of bentonite. On the other hand, high percentages of bentonite gave less compact pastes that could fall off the electrode with the rotation movement.

Taking into account these results, a bentonite percentage of 5% was chosen. This proportion does not give the maximum i_p, but it reduces the residual current and peak width, and eliminates paste loss.

Effect of the Rotation Rate, Pulse Amplitude and Temperature

The use of a rotating carbon paste electrode improves the sensitivity and the peak shape compared with a stationary electrode. The intensity increase is very high in the range 0–1000 rev min^{-1}, a slight and continuous increment is observed from 1000 to 3000 rev min^{-1} (Fig. 4).

The measurements were always carried out at room temperature. The temperature variations (15–25 °C) made negligible differences to the intensity (Fig. 4).

The i_p shows a linear relationship with the pulse amplitude, ΔE, in the range 0 to − 100m V (Fig. 5). The value of − 100 m V was chosen, as it gave the highest sensitivity. The selectivity is not affected by the small variations of the peak width.

Calibration Graph

A linear relationship exists between i_p and the concentration in the range 0.07–10 mg l^{-1} ($r = 0.9999$) with a slope of 3.1 μA 1 mg^{-1} and an intercept of 0.08 μA. The detection limit [23, 24] is 0.03 mg l^{-1}; statistical treatment of the results obtained by eleven determinations of 5 mg l^{-1} concentration gave a relative standard deviation of 1.8%, and a relative error of − 1.9%.

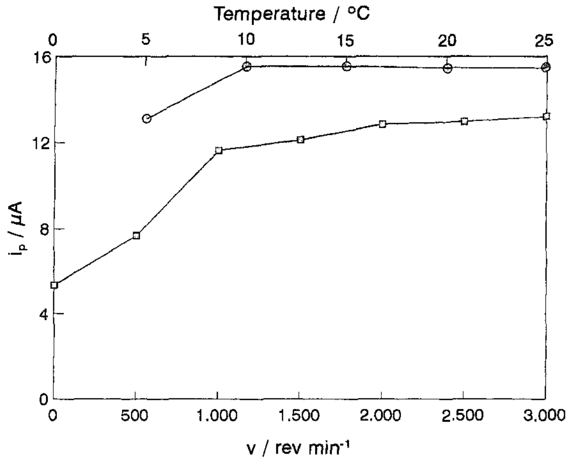

Fig. 4. Influence of rotation rate (■) and temperature (●) on i_p for a 2-nitrophenol concentration of 5 mg l^{-1} at a 5% bentonite-modified electrode

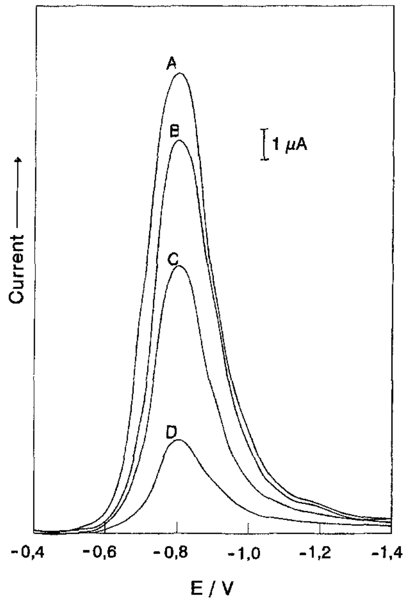

Fig. 5. Voltammograms for different pulse amplitudes for a concentration of 5 mg l^{-1}: *A* 100, *B* 80, *C* 50 and *D* 10 m V

Interferences

Several nitro- and chlorophenols were tested for their influence on the 2-nitrophenol signal. The interferent: 2-nitrophenol mass ratios studied were 5:1 and 1:1. The results show, as expected, that the nitrophenols interfere with the 2-nitrophenol determination, specially at the 5:1 ratio. For 4-nitrophenol and 2,4-dinitrophenol the analyte can be detected selectively according to their peak potentials at a 1:1 mass ratio. The E_p for 4-nitrophenol (− 1.0 V) is more negative than for 2-nitrophenol (− 0.8 V), and the signal for 2-nitrophenol can be adequately measured. For 2,4-dinitrophenol (peak potentials − 0.4 and − 0.7 V) the second peak is smaller than the first, and 2-nitrophenol is detected without interference. Picric acid and 2-methyl-4,6-dinitrophenol also produce two peaks (peak potentials − 0.3/− 0.9 and − 0.4/− 0.7 V respectively), but the peaks for these compounds are higher than for 2,4-dinitrophenol. For this reason, the differences of the second peak potentials with respect to the peak potential for 2-nitrophenol are not enough to obtain good resolution, and high deviations are observed.

The chlorophenols caused only small deviations (below 10%). These compounds are easily oxidized and their cathodic activity is smaller than for the nitrophenols. In the experimental conditions used, chlorophenols were either not active or gave small signals which did not cause high deviations.

Table 2. Effect of inorganic and organic species on the determination of 2-nitrophenol

Interferent	Interferent:2-nitrophenol mass ratio	Deviation (%)
Ni^{2+}	5:1	−1.4
Co^{2+}	5:1	+8.6
Zn^{2+}	1:1	−3.3
Mn^{2+}	1:1	−5.7
Al^{3+}	1:1	−1.9
Cr^{3+}	5:1	−0.7
Fe^{2+}	5:1	+8.6
Fe^{3+}	1:1	+29.3
Pb^{2+}	1:1	−23.8
Cu^{2+}	1:1	+10.9
NH$_4^+$	5:1	+2.6
SiO$_3^{2-}$	1:1	−2.4
NO$_3^-$	1:1	−1.0
CO$_3^{2-}$	1:1	+1.0
PO$_4^{3-}$	5:1	+6.8
Picric acid	1:1	+19.0
2,4-Dinitrophenol	1:1	−1.4
4-Nitrophenol	1:1	−0.8
2-Methyl-4, 6-dinitrophenol	1:1	+30.9
2,4,6-Trichlorophenol	5:1	+5.2
Pentachlorophenol	5:1	+6.2
2,4-Dichlorophenol	5:1	+3.1
4-Chloro-3-methylphenol	5:1	+7.3

The possible interference of several inorganic species was also ivestigated. At the 1:1 ratio only Pb^{2+}, Cu^{2+} and Fe^{3+} caused significant deviations. At the 5:1 ratio there are more interferent species (Al^{3+}, CO$_3^{2-}$, NO$_3^-$, SiO$_3^{2-}$, Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+} and Zn^{2+}) and in the case of Pb^{2+} the 2-nitrophenol signal disappears. The results are shown in Table 2.

Determination of 2-Nitrophenol in Sea Water

Several sea water samples were spiked with 2-nitrophenol. The analytical solutions placed into the electrochemical cell had 2-nitrophenol concentrations in the range 0.1–5 mg l^{-1}. The results show excellent recoveries of 103, 96 and 99% for 0.5, 1 and 5 mg l^{-1}, respectively. For a 0.1 mg l^{-1} 2-nitrophenol concentration a recovery of 107% was obtained.

Conclusions

The modified carbon paste electrode described in this paper is very cheap and easy to prepare and replace, and it can be used both for reductions and for oxidations, similar detection limits are obtained when the same electroanalytical technique and a mercury electrode are used for reduction processes [13]. The detection limit is smaller than those reported for flow systems at a mercury electrode [7] and for polarographic determination [10]. Only the use of more sensitive techniques [13] or more complex electrodes [14] can improve the limits of the determination. A wide variety of configurations are available for this carbon electrode: polymeric coatings incorporation of modifiers into the carbon paste (clays, ion-exchange resins, etc.), use of enzymes, applications in flow systems and in HPLC detection, that can improve the sensitivity and selectivity of the determinations.

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