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Voltammetric study of 2-methyl-4,6-dinitrophenol at a modified carbon paste electrode

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Abstract

The voltammetric behavior of 2-methyl-4,6-dinitrophenol at a modified carbon paste electrode has been studied. Among the modifiers tested, hidepowder was found to give the best results. Cyclic voltammetry and differential pulse voltammetry were used to study the nature of the reaction; the possibility of accumulation of the analyte onto the electrode was studied by differential pulse voltammetry. An irreversible behavior and the adsorption of 2-methyl-4,6-dinitrophenol on the electrode were confirmed. The reduction signal shows two peaks. A linear relationship between the first peak height and the concentration of 2-methyl-4,6-dinitrophenol was obtained in the range 0.001–5 mg l^{-1}, with a detection limit of 3.2 μg l^{-1} and a relative standard deviation of 3.20%. The interferences with the reduction peak of 2-methyl-4,6-dinitrophenol of several nitro- and chloro-phenols and inorganic species were tested.

Keywords: 2-methyl-4,6-dinitrophenol; Differential pulse voltammetry; Hidepowder-modified carbon paste electrode

1. Introduction

Dinitrocompounds are considered to be specially important compounds since they show a highly toxic effect in every form of life [1]. These substances are used in their pure form or combined with others in a wide variety of pesticides, even being classified as prioritant pollutants by the US Environmental Protection Agency (EPA). 2-Methyl-4,6-dinitrophenol is one of the dinitrophenols included in the EPA list of priority pollutants [2]. It finds an extensive use as an insecticide and is formed as a side reaction product, in the manufacturing process of nitrotoluene isomers [3]. 2-Methyl-4,6-dinitrophenol can be tolerated in a concentration (TWA, time weighted average) up to 0.17 mg kg^{-1} without prejudicial effect in humans [4].

Dinitrophenols have been determined by different techniques such as liquid chromatography (LC) [5,6], and gas chromatography with mass spectrometry or flame ionization detection [7,8]. Differential pulse voltammetry and adsorptive stripping voltammetry have also been applied to the determination of dinitrophenols [9]. Some differential pulse polarographic methods have been described for the determination of 2-methyl-4,6-dinitrophenol [1,10,11].

Carbon paste electrodes give better results than other solid electrodes because of their low residual

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current and noise, their ease to prepare and replace, and their wide anodic and cathodic potential ranges. Modified carbon paste electrodes have been studied to maintain these advantages but remove most of their drawbacks [12,13]. In this paper, hidepowder is tested as modifier for the carbon paste. Hidepowder is a natural product made of calf skin mainly used in the leather manufacturing industry. Subsequently, the nature of the reaction was studied using differential pulse voltammetry and cyclic voltammetry. Furthermore, the possible accumulation of the analyte onto the electrode was investigated.

2. Experimental

Apparatus. A Metrohm E-506 Polarecord coupled to a 663VA Stand was used for voltammetric experiments, with a rotating carbon paste working electrode (surface area 7 mm^2), a silver/silver chloride reference electrode and a platinum auxiliary electrode.

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 required amount of the modifier to obtain the desired mass proportion. The resulting paste was packed into the electrode and the surface was smoothed. After each measurement, the paste was removed and the cavity of the electrode was cleaned with water and dried with a tissue. A Britton–Robinson buffer was used for the pH studies, and this and other buffers with several ionic strengths at the optimum pH value were also tested. Different pH values were obtained by addition of 1 M NaOH. 2-Methyl-4,6-dinitrophenol stock solutions (5 g l^{-1}, Supelco, analytical reagent grade) were prepared in ethanol (Merck, analytical reagent grade). Working solutions were prepared daily by dilution with distilled water. Spectroscopic graphite was obtained from Ringsdorff-Werke GMBH, Bonn, Germany; mineral oil from Sigma; zeolite and bentonite from Aldrich and hidepowder from Merck.

2.1. Procedures

2.1.1. Voltammetric procedure for the study of variables

A volume of 25 ml of buffer solution was placed in the cell. After purging with nitrogen for 15 min, a differential pulse voltammogram was recorded. After addition of 50 μl of the 2-methyl-4,6-dinitrophenol solution, a new voltammogram was obtained and the paste was then removed from the electrode; the cleaning and packing procedures were repeated before each measurement. From these initial conditions, the study of each variable was made, using each optimized value in the subsequent study. For the study of the temperature, a cell with thermostatic jacket was used. For the accumulation studies, the hidepowder-modified carbon paste electrode was placed in the cell containing the stirred 2-methyl-4,6-dinitrophenol solution and the accumulation time and potential were studied. Calibration and study of interferences were carried out under the operating conditions obtained through the study of variables: 10% hidepowder-modified carbon paste electrode; pulse amplitude, −100 mV; pulse repetition time, 0.8 s; working electrode rotation rate, 1500 r.p.m.; formic acid/sodium formate buffer solution (pH 4, ionic strength 0.05) and a temperature of 25°C. The nature of the reduction reaction was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV); the same procedure described previously was used and the experiments were carried out under the operating conditions used for calibration graph and the study of interferences. Scan rate (CV), pulse amplitude, accumulation potential and accumulation time (DPV) were the parameters tested.

3. Results and discussion

3.1. Influence of modifier

The peak height (i_p) and peak potential (E_p) using unmodified carbon paste, zeolite-modified carbon paste (5%), bentonite-modified carbon paste (5%) and hidepowder-modified carbon paste (5%) were studied. In all cases, 2-methyl-4,6-dinitrophenol shows a higher peak at −0.3 V and a lower peak at −0.6 V. The i_p and E_p values are shown in Table 1. The differences between values obtained using hidepowder and values obtained using zeolite, bentonite or no modifier led to the selection of hidepowder as modifier of the carbon paste for the latter studies.

Table 1
Influence of modifier used on peak height (i_p) and peak potential (E_p) (concentration of 2-methyl-4,6-dinitrophenol (5 mg l^{-1}))

Modifier	i_{p1} (μA)	i_{p2} (μA)	E_{p1} (V)	E_{p2} (V)
None	5.3	1.0	−0.32	−0.60
Zeolite (5%)	5.0	1.1	−0.32	−0.57
Bentonite (5%)	5.6	1.3	−0.32	−0.54
Hidepowder (5%)	6.2	1.6	−0.29	−0.57

3.2. Influence of pH

Studies on the effect of pH were carried out at a 2-methyl-4,6-dinitrophenol concentration of 5 mg l^{-1} at pH 1.7–11 with a Britton–Robinson buffer solution. The first peak potential, E_{p1}, shows a clear dependence on pH, with two linear regions with different slopes, and an intersection point at pH 3.88, which agrees [14] with the pK_a of 2,4-dinitrophenol [15], i.e. a compound of an acid behavior similar to that of 2-methyl-4,6-dinitrophenol. In the range 1.7–9, the two peaks are clearly distinguished [1,3,16]. The first peak nearly disappears at pH 10, being completely lost at pH 11. The second peak never disappears. A third peak (more negative that the second one) began to appear at pH 9–10, disappearing at pH 12. The peak heights reach their maximum value in acidic media. Fig. 1 shows the influence of pH on E_p and i_p for the first peak in the range 1.7–9 where well-defined peaks were obtained. The highest peak was obtained for pH 4.

3.3. Influence of buffer solution

Several buffer solutions of pH 4 at different ionic strengths (I) were tested to study the effect on the 2-methyl-4,6-dinitrophenol determination. These results are shown in Table 2. No significant differences were observed in peak potentials with variations of ionic strength for a given buffer. However, E_p values are not the same between different buffers. The peak height varies for each buffer and for each ionic strength. There are two cases which offer better results: formic acid/sodium formate (I=0.05) and acetic acid/sodium acetate (I=0.05). Because the first gives a better resolution of the two peaks the formic acid/sodium acetate buffer solution with an ionic strength of 0.05 and pH 4 was chosen.

3.4. Influence of percentage of hidepowder

Proportions up to 10% were studied and higher values were not used because the mixtures obtained

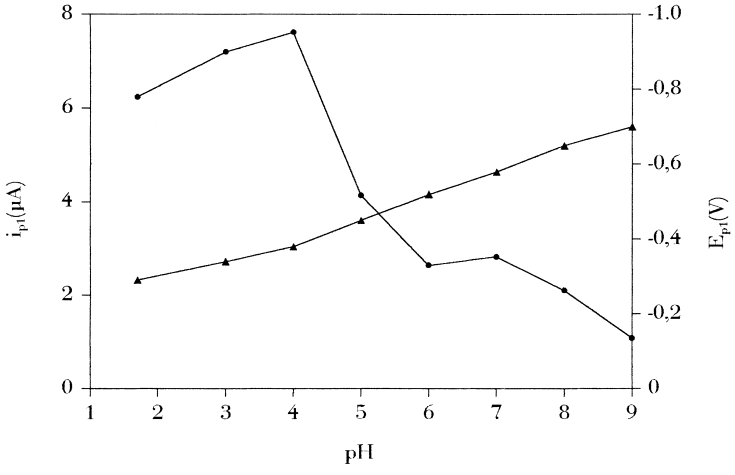

Fig. 1. Influence of pH on E_{p1} (▲) and i_{p1} (●) for a 5 mg l^{-1} 2-methyl-4,6-dinitrophenol concentration at a 5% hidepowder-modified carbon paste electrode. Pulse amplitude (−50 mV); pulse repetition time (0.4 s); rotation rate (1500 r.p.m.).

Table 2
Variation of peak height and peak potential with different buffers and different ionic strenghts at pH 4 (concentration of 2-methyl-4,6-dinitrophenol (5 mg l^{-1}))

Buffer solution (pH 4)	I (dimensionless)	i_{p1} (μA)	i_{p2} (μA)	E_{p1} (V)	E_{p2} (V)
Formic acid/sodium formate	0.05	6.4	2.5	−0.44	−0.70
Formic acid/sodium formate	0.1	5.4	2.1	−0.46	−0.70
Formic acid/sodium formate	0.2	5.0	1.8	−0.44	−0.70
Acetic acid/sodium acetate	0.05	6.5	2.5	−0.5	−0.73
Acetic acid/sodium acetate	0.1	6.0	2.4	−0.5	−0.74
Hydrochloric acid/potassium ftalate acid	0.025	5.3	2.0	−0.5	−0.78
Hydrochloric acid/potassium ftalate acid	0.05	5.2	1.8	−0.5	−0.77
Britton–Robinson	0.0025	5.0	1.8	−0.52	−0.76
Britton–Robinson	0.005	5.4	2.0	−0.48	−0.76
Britton–Robinson	0.01	4.9	1.7	−0.48	−0.76
Britton–Robinson	0.025	6.2	2.1	−0.51	−0.76
Britton–Robinson	0.05	5.7	2.0	−0.51	−0.76

were less compact and could fall off the electrode on rotation. The highest peaks were obtained with 10% of hidepowder in the carbon paste.

3.5. Effect of rotation rate, pulse amplitude and temperature

The application of rotation to the working electrode improves its sensitivity because of the vertical flux aimed towards the base surface of the electrode where the rotation originates. Peak height increases in the range 0–2000 r.p.m. but it decreases in the range 2000–3000. A distortion in the second peak was observed, beginning slightly at 1000 r.p.m. and increasing considerably from 2000 r.p.m. For this reason, 1500 r.p.m. was chosen as the working electrode rotation rate.

The i_{p1} shows a linear relationship with the pulse amplitude, ΔE, in the range from 0 to −100 mV (i_{p1} (μA)=−2+0.177|ΔE|(mV); r=0.9974). The value of −100 mV was chosen, as it gave the highest sensitivity.

The effect of temperature was assessed in the range 11.3–36.3°C. Between 25°C and 30°C the peak height rises only by 2 μA, but in the range 30–36°C the increase is by 9 μA. Although high temperatures gave better results, they are not recommended because of the possibility of a partial vaporization of the cell solution. A temperature of 25°C was selected.

3.6. Study of the nature of the reaction

Reduction of 2-methyl-4,6-dinitrophenol at the electrode was studied using cyclic and differential pulse voltammetry. The experiments were performed using a concentration of the analyte in the cell of 5 mg l^{-1}. Differential pulse voltammetry was also used to investigate the possibility of accumulation on the electrode.

3.6.1. Cyclic voltammetry

The variation of the peak intensity and the peak potential with the scan rate was studied. An approximately linear relationship was found between the first peak intensity, i_{p1}, and the square root of the scan rate, v_b (i_{p1} (μA)=−0.66+26.68 $v_b^{1/2}$ (r.p.m.); r=0.9808) and the peak potential was found to move slightly more negative when the scan rate increased in agreement with the irreversible behavior of the test substance (see Fig. 2).

3.6.2. Differential pulse voltammetry

The influence of a variation of the pulse amplitude on the peak height and the peak potential has been studied. A correlation coefficient of 0.997 was obtained between the first peak height and the pulse amplitude and there was also an increase of the peak potential with the pulse amplitude [17], in agreement with a practically irreversible behaviour.

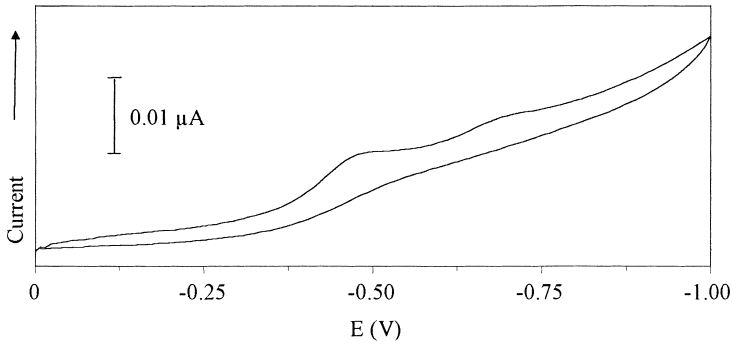

Fig. 2. Cyclic voltammogram of 2-methyl-4,6-dinitrophenol (concentration 5 mg l^{-1}) at a 10% hidepowder-modified carbon paste electrode, scan rate=0.025 V s^{-1}.

The possible accumulation of 2-methyl-4,6-dinitrophenol on the working electrode was also investigated. A concentration in the cell of 1 mg l^{-1} was used. The influence of the accumulation potential in the peak height was determined, applying 5 min of accumulation. 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 (0.2, 0, −0.2, −0.4). The maximum peak height was obtained imposing an accumulation potential of 0 V, so that this was the potential used in the study of the accumulation time. A range of 0–20 min was studied and the measurements were carried out under the previously optimized conditions. Results are shown in Fig. 3. The observed dependence can be explained by a saturation of the electrode surface with the analyte after a long accumulation time. A period of 17 min has been chosen as an optimum to be applied in further experiments with accumulation. Fig. 4 shows the difference between the signal corresponding to an accumulation time of 17 min and the signal without accumulation.

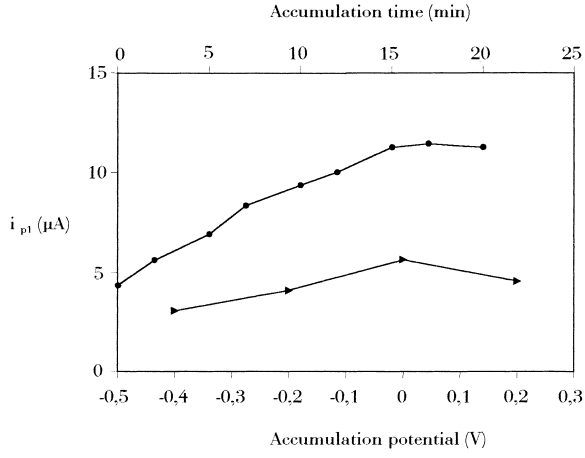

Fig. 3. Influence of accumulation time (■) and accumulation potential (▲) on i_{p1} for a 2-methyl-4,6-dinitrophenol concentration of 1 mg l^{-1} on the height of the first peak.

3.7. Calibration graph

A linear relationship between i_{p1} and the concentration in the range 0.001–5 mg l^{-1} has been found (r=0.9996) with a slope of 3.6 µA l mg^{-1} and an intercept of −0.11 µA. The detection limit obtained in a range of concentration of 0.001–0.1 mg l^{-1} is 3.2 µg l^{-1}. Statistical treatment of the results obtained by nine determinations of 1 mg l^{-1} concentration gave a relative standard deviation of 3.20% and a relative error of 3.05%.

The calibration graph was also studied applying accumulation. The range 0.01–0.5 mg l^{-1} was analyzed and the main effect observed was that the second peak was very distorted by the signal of the background (nearly disappeared) and the resolution of the peaks worsens for the lower concentrations, and for 0.01 mg l^{-1} the effect is so that the second peak is hidden by the background and the first peak is fairly distorted. This fact causes a fairly large increase

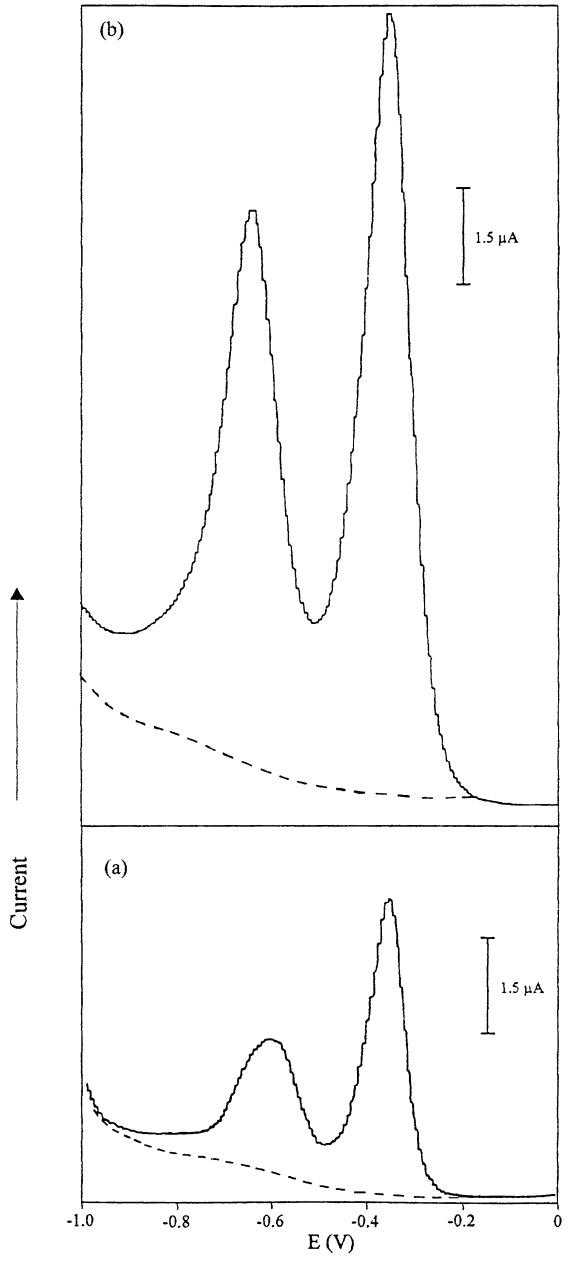

Fig. 4. Differential pulse voltammograms for a 1 mg l^{-1} 2-methyl-4,6-dinitrophenol concentration: (a) without accumulation and (b) with an accumulation time of 17 min. Signals of background (- - -) are also shown.

in the detection limit (0.05 mg l^{-1}). Therefore, the accumulation step is generally not recommendable to be applied.

3.8. Interferences

The possible influence of several nitro- and chlorophenols on the reduction signal of 2-methyl-4,6-dinitrophenol was considered. An initial interferent:2-methyl-4,6-dinitrophenol mass ratio of 5:1 was tested, which was decreased when an interference was observed. Picric acid and 2,4-dinitrophenol show a clear interference on both peaks, which becomes less when the ratio interferent:2-methyl-4,6-dinitrophenol decreased. However, 2-nitrophenol and 4-nitrophenol, cause large deviations. For 4-nitrophenol, in the ratio 5:1, this deviation is due to a great effect on the more negative peak of 2-methyl-4,6-dinitrophenol, so a direct influence on the first peak does not exist. In the case of 2-nitrophenol, there is a similar effect, except that the interference occurs at a less negative potential and the first peak appears as a shoulder of the 2-nitrophenol peak. When the ratio decreased to 1:1, the effect decreases so the first peak of 2-methyl-4,6-dinitrophenol is clearly distinguished. Chlorophenols caused deviations below 10% because they are practically inactive under the experimental conditions used. The possible interference of various inorganic species was also analyzed; at the ratio 5:1 only for Cu^{2+} and Pb^{2+} significant deviations were observed, which are smaller for the ratio 1:1, especially in the case of Pb^{2+}. Results are shown in Table 3.

The accumulation step might be useful in the case of the existence of an interferent, because if it does not collect onto the modified carbon paste, the signal of the analyte will be less or not affected at all by the interferent, as in the case of Cu^{2+}, Pb^{2+}, 2-nitrophenol and 4-nitrophenol with a concentration in cell of 5 mg l^{-1}, because they do not accumulate on carbon paste under the experimental conditions used.

Consequently, although the accumulation step does not improve the detection limit, it can be used to avoid the effect of some interferents.

The method for the determination of 2-methyl-4,6-dinitrophenol was applied to river water and sea water samples. No signal for 2-methyl-4,6-dinitrophenol was observed when the samples were analyzed. Thus, the method was applied to samples spiked with 2-methyl-4,6-dinitrophenol. The results for river water showed very good recoveries of 98%, 100%, 100% and 105.6% for 1, 0.5, 0.1 and 0.05 mg l^{-1}, respectively. For sea water, values of 92%, 107%, 94.2% and

Table 3
Effect of inorganic and organic especies on the determination of 2-methyl-4,6-dinitrophenol at a concentration of 1 mg l^{-1}

Interferent	Interferent:analyte mass ratio	Deviation (without accumulation (%))	Deviation (with accumulation (%))
2,4-Dichlorophenol	5:1	1.51	—
4-Chloro-3-methylphenol	5:1	2.85	—
Pentachlorophenol	5:1	4.31	—
2,4,6-Trichlorophenol	5:1	6.75	—
Picric acid	5:1	>100	25.9
	1:1	61.22	—
	0.5:1	21.42	—
2,4-Dinitrophenol	5:1	>100	>100
	1:1	76.40	31.6
	0.5:1	23.94	—
2-Nitrophenol	5:1	−19.35	9.7
	1:1	−32.81	1.5
4-Nitrophenol	5:1	−9.10	6
Ni^{2+}	5:1	0	—
Co^{2+}	5:1	5.48	—
Zn^{2+}	5:1	5.56	—
Mn^{2+}	5:1	4.62	—
Al^{3+}	5:1	4.84	—
Cr^{3+}	5:1	3.88	—
Pb^{2+}	5:1	32.35	3.4
	1:1	1.40	—
Cu^{2+}	5:1	17.65	4.3
	1:1	7.04	—
Fe^{2+}	5:1	9.30	—
Fe^{3+}	5:1	10.00	—
NH_4^+	5:1	0	—
$SiO_3^=$	5:1	0	—
NO_3^-	5:1	2.73	—
$CO_3^=$	5:1	1.40	—
PO_4^{3-}	5:1	5.35	—

108.3% were obtained for 5, 1, 0.5 and 0.1 mg l^{-1}, respectively.

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