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Use of a carbon paste modified electrode for the determination of 2-nitrophenol in a flow system by differential pulse voltammetry

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Abstract

The electrochemical reduction of 2-nitrophenol at a bentonite-modified carbon paste electrode by rapid scan differential pulse voltammetry in a flow system is studied, and a method for the direct voltammetric determination in sea water is proposed. A formic acid/sodium formate buffer solution of pH 4 was used as carrier. The potential range and the scan rate were selected according to the response of the analyte. 2-Nitrophenol showed a reduction potential within the cathodic range for the carbon electrode; a well-defined single peak was obtained. It is not necessary to remove the paste from the electrode after each new injection because the surface activity of the electrode remained constant at least during the time of a single complete analysis. A linear relationship between peak height and concentration was obtained in the range 0.05–5 mg l^{-1} with a detection limit of 0.02 mg l^{-1} and a relative standard deviation of 3.6%. Several chloro- and nitrophenols were tested to assess their influence on 2-nitrophenol signals.

Keywords: Differential pulse voltammetry; Flow system; Carbon paste modified electrode; 2-Nitrophenol

1. Introduction

The interest in the determination of phenols in environmental samples has prompted the development of a variety of methods for their quantification. Phenols are common in industrial effluents, and the simple phenols are easily degraded, and analysis must be done promptly. 2-Nitrophenol is one of the nitrophenols included in the US Environmental Protection Agency List of Priority Pollutants [1,2]. A liquid chromatographic method for measuring in waste streams the chloro- and nitrophenols included in the Priority Pollutants List using dual-wavelength UV detection has been described [3].

The use of different electroanalytical techniques has been also described: polarography, a.c. polarography, cyclic voltammetry, adsorptive stripping voltammetry [4–7]. The use of C_{18} in a carbon paste electrode for the determination of nitrophenols has been recently reported [8].

Electrochemical techniques have been applied in flowing streams to environmentally important reducible molecules, for example, aromatic nitro compounds. These methods compare favorably with the usual gas chromatographic methods. Electrochemical detection of 2-nitrophenol and other nitrophenols by a.c. and square wave voltammetry in liquid chromatography (LC) has been described using a mercury electrode [9–11]. Differential pulse technique has been used in stripping voltammetry at a mercury

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electrode in a flow injection system [12–14]. Applications to reduction reactions are generally considered to be more difficult than to oxidation reactions because of higher background currents from the reduction of hydrogen ions and oxygen.

Voltammetric methods are particularly suited to the analysis of a wide variety of organic compounds. Non-stationary voltammetric methods, of which alternating current, square wave, pulse and differential pulse are most widely used, have been introduced in an attempt to improve the sensitivity and selectivity of the measurements. A possibility offered by non-stationary methods is the simultaneous resolution of the analytes in two domains, time and voltage, by using rapid scan voltammetric techniques [15]; these techniques also make it possible to determine readily the optimal conditions for the detection of the individual sample components.

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; these electrodes have a wide range of anodic and cathodic applicability. To retain the advantages of carbon paste electrodes and remove most of their drawbacks, modified carbon paste electrodes have been studied, including exchanger resins and clays [16–20]. The bentonites exhibit similar properties to those of other clays. 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 by rapid scan differential pulse voltammetry in a flow system is studied, and a method for the direct voltammetric determination of this compound in sea water is proposed. The modified carbon paste electrode could also be used as electrochemical detector for liquid chromatography, so substantially improving the selectivity of the determinations, as has been described for a wide variety of compounds [21].

2. Experimental

2.1. Apparatus

The flow injection system consisted of a Gilson Minipuls-2 peristaltic pump and a Rheodyne 5020 sample injection valve with variable injection volumes. The exact flow rate must be measured at the outlet of the flow stream by collecting a fixed volume of effluent. The electrochemical cell was a Metrohm 656 Electrochemical Detector equipped with a carbon paste working electrode (surface area 7 mm^2), a silver/silver chloride reference electrode and a gold auxiliary electrode. The differential pulse mode was performed by means of a Metrohm 611 Detector coupled to a Metrohm 612 Scanner; with this electrochemical device the rapid scan differential pulse voltammetry measurements were carried out. The voltage pulse was applied with a duration of 60 ms. The pulse amplitude could be preselected. The injection system was connected to the flow cell through 0.5 mm i.d. PTFE tubing. The *x–y*/*x–t* signals were registered on a Hewlett–Packard Model 862/D X–Y recorder. All measurements were carried out at room temperature.

2.2. 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 bentonite at a percentage of 5%. 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. After a single complete analysis the paste was removed and the cavity of the electrode was cleaned and dried.

Oxygen was removed by purging with nitrogen both carrier and sample solution before and during the analysis time.

Artificial sea water was prepared by dissolving different salts in 1 l 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). A formic acid/sodium formate buffer solution of pH 4 was used as carrier solution.

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

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

2.3. Procedures

Initial procedure: A formic acid/sodium formate buffer solution of pH 4 was used as carrier, and artificial sea water with a pollutant concentration of 5 mg l^{-1} was used as sample. After purging with nitrogen, 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 differential pulse voltammetry or d.c. amperometry at a carbon paste electrode containing 5% of bentonite. Artificial sea water was used as blank.

The data were registered in different types of plots. The *i/E* recordings were obtained for stopped flow voltammograms. When the flow injection system was used, *i/t* recordings were obtained.

When the potential scan rate is fast the voltammogram of the dispersed sample is similar to the voltammogram of a stationary solution. Then the *i/t* plots can be obtained by means of a rapid scanning instrument (where intensity is measured continuously within a certain potential range along the dispersed sample zone). If this is not the case, the maximum of the flow peak can be stopped in the detector, and a stopped flow voltammogram is obtained.

A hydrodynamic voltammogram was obtained by injection of the sample into the carrier solution and measuring the current at a single potential between −0.2 and −1.2 V. The heights of the flow peaks measured at each applied potential and the hydrodynamic voltammogram of the blank solution were obtained.

For the stopped flow voltammograms, a volume of 0.25 ml of the sample (2-nitrophenol 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. The voltammograms were registered at different scan rates, from 50 to 200 mV s^{-1}, in the differential pulse mode.

The three-dimensional set of voltammograms was carried out between −0.2 and −0.9 V at a scan rate of 20 mV s^{-1}. Voltammograms were recorded every second, and by means of stopped flow injections.

For the electrode study, repeated injections were carried out without removing the paste from the electrode in order to verify that the electrode surface is in a reproducible active state. The injection frequency depended on the peak width.

For the optimization studies, a differential pulse technique was used. Calibration graph and study of interferences were carried out by the operating conditions obtained through the study of variables: scan rate 400 mV s^{-1}; potential range from −400 to −600 mV; pulse amplitude −75 mV; pulse repetition time 0.2 s; injected volume 0.75 ml; flow rate 1.75 ml min^{-1}.

The proposed method was applied to sea water samples spiked with the 2-nitrophenol solution. The determinations were carried out by the operating conditions described for the calibration graph and the study of interferences. The results were compared with a well-established technique.

3. Results and discussion

The stopped flow voltammograms of 2-nitrophenol for two scan rates are shown in Fig. 1. 2-Nitrophenol showed a reduction potential within the cathodic range for the carbon electrode; a well-defined single peak was obtained, and the peak heights were higher than those obtained by amperometric detection. An increase in the signals was observed with increasing scan rate.

Hydrodynamic voltammograms from 5 mg l^{-1} of 2-nitrophenol and from blank solution are shown in Fig. 1. The data of the peak heights with blank substraction are also shown; a well-defined plateau was obtained from −0.7 to −0.9 V with a value of 3.75 µA.

In a three-dimensional set of voltammograms the reduction of 2-nitrophenol on the bentonite modified carbon paste electrode, and the voltammograms and the concentration gradient profile can be observed simultaneously. The peak is located at a potential at which the reduction process occurs and with a peak height related to the concentration gradient.

In order to obtain the optimum *i/t* plots, the influence of scan rate and potential range was studied. Since fast scans were carried out continuously, each *i/t* peak was composed of as many sweeps as could be performed during the passage of the sample through the detector. Because the fast scans are performed continuously, it could be ensured that several scans had been run at the maximum of the flow peak

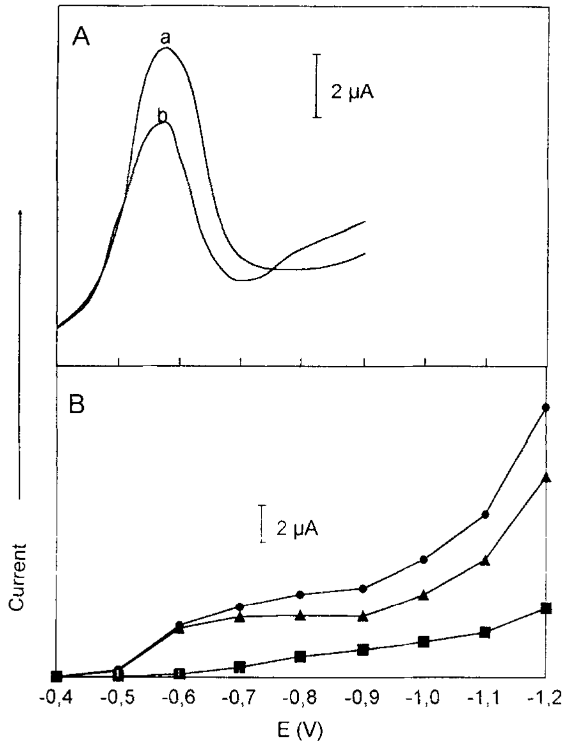

Fig. 1. (A) Stopped flow differential pulse voltammograms for a 5 mg l^{-1} 2-nitrophenol solution at different scan rates: (a) 100 and (b) 50 mV s^{-1}. (B) Hydrodynamic voltammograms from (●) 5 mg l^{-1} of 2-nitrophenol and from (■) blank solution. Peak height with blank substraction (▲) is also shown.

(the measurement interval was sufficiently short). For example, the voltammetric variables used for the calibration graph were a scan rate of 400 mV s^{-1} and a potential range from −400 to −600 mV; the extrapolated peak width was about 32 s. Under these conditions, two scans could be completed every 1 s (0.5 s $scan^{-1}$) and 64 scans could be run during the passage of the sample.

According to Fig. 1, a peak potential of about −0.575 V was obtained, and a potential range between −0.4 and −0.6 V gave the maximum peak height. An increase in peak height was observed with increasing scan rate. For 400 mV s^{-1} the potential sweep was completed in 0.5 s.

The effect of the pulse amplitude, ΔE, was studied over the range from −25 to −250 mV. Peak height increased with increasing ΔE up to −150 mV, after which it remained virtually constant. A linear relationship between peak height and ΔE was obtained in the range from −25 to −75 mV. On the other hand, the optimum signal to noise ratio was obtained for ΔE=−75 mV; this value was used for subsequent experiments. The *i*/*t* plots obtained for different pulse amplitudes are shown in Fig. 2.

Flow injection variables must be selected to achieve a suitable peak width to run the voltammetric scans, without an excessive decrease of the sampling capacity; the sensitivity (peak height) of the response must also be considered.

Peak height and peak width in flow systems depend on the dispersion of the sample during its passage from injector to detector. Fig. 3 shows the effect of flow rate and injection volume on i_p. The peak width and the residence time decreased with increasing flow rate,

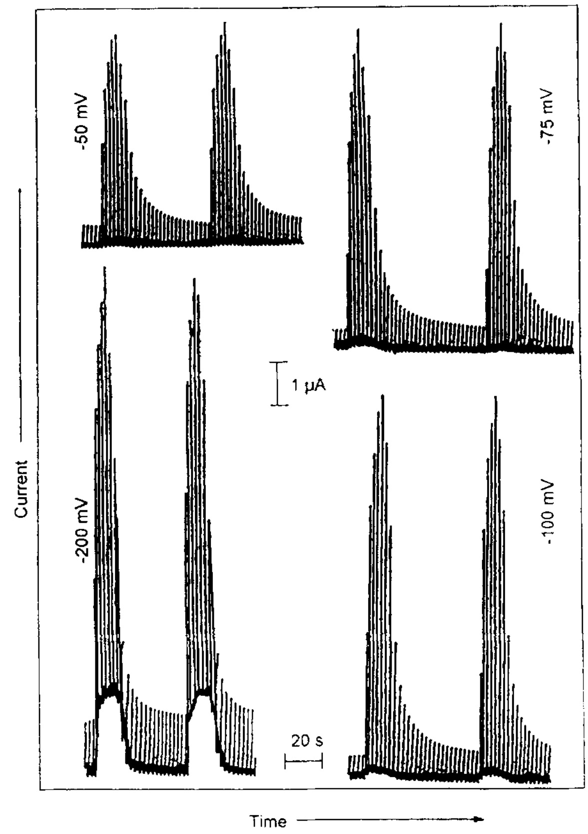

Fig. 2. *i*/*t* plots for a 5 mg l^{-1} 2-nitrophenol solution at different pulse amplitudes. Scan rate 400 mV s^{-1}; potential range from 400 to 600 mV; flow rate 1.25 ml min^{-1}; injected volume 0.25 ml.

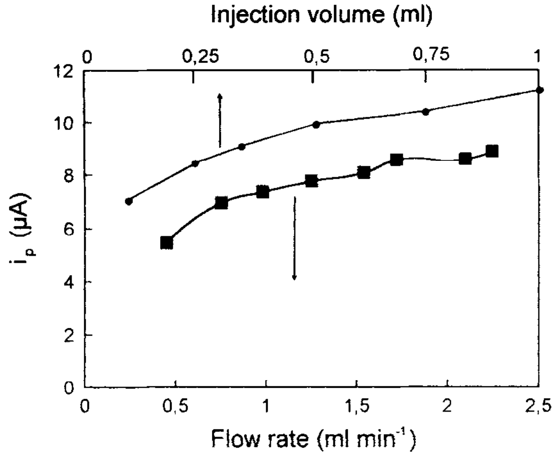

Fig. 3. Effect of injection volume (●) and flow rate (■) on i_p for a concentration of 5 mg l^{-1} of 2-nitrophenol. Scan rate 400 mV s^{-1}; potential range from 400 to 600 mV; pulse amplitude −75 mV.

whereas they increased with increasing injection volume. An increase in the signal was observed as the flow increased from 0.4 to 2.25 ml min^{-1}; a value of 1.7 ml min^{-1} gave the best signal to noise ratio, and this flow rate was used for further studies. Similar variation of the peak height was found for injection volume in the range 0.1–1 ml. When an injection volume of 0.25 ml was used, a peak height of 8.5 µA was reached and a sampling frequency of about 90 h^{-1} was obtained. If an injection volume of 0.75 ml was used, an increase on peak height was observed (9.8 µA), and according to the peak width a sampling capacity of about 70 h^{-1} was obtained. In both cases the peak width ensured sufficient time to run the voltammetric scans. In order to improve the sensitivity without an excessive decrease of sampling capacity, a sample loop of 0.75 ml was chosen. For these conditions, the residence time was 20 s and the extrapolated peak width 32 s. The sample volume was diluted by a factor of 0.8 as estimated from the extrapolated peak width expressed in volume units (0.9 ml); so then, the system could be considered as a limited dispersion system [22]. The current reached its baseline value about 50 s after an injection, allowing a sampling frequency of about 70 h^{-1}. The tube length between injection valve and detector could be kept as short as possible (40 cm) because no chemical reaction was involved.

3.1. Stability of the electrode surface

The 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 with the carrier liquid and is exposed only to relatively short analyte zones.

High percentages of bentonite produce an increase in the residual current and give less compact pastes that could fall off the electrode with the flow stream. A bentonite percentage of 5% was used to reduce the residual current and to eliminate the possibility of paste loss.

The use of a carbon paste electrode in the detector cell and its application to a flow injection system results in a constant surface activity of the working electrode, at least during the time of a single complete analysis. In our experiments, a good stability of the electrode surface was observed; after a series of repeated injections (n=16) at a fixed frequency according to the peak width of the analyte, the peak intensity remained practically constant. A mean value of 8.21 µA and a relative standard deviation of 1.05% were obtained. Thus, it was not necessary to remove the paste from the electrode after each new injection.

3.2. Calibration graph

Peak heights were linearly related to 2-nitrophenol concentration over the range 0.05–5 mg l^{-1} (r=0.9996) with a slope of 1.8 µA l mg^{-1} and an intercept of 0.8 µA. The detection limit [23,24] was 0.02 mg l^{-1}, and a relative standard deviation of 3.6% was obtained for eleven injections of 1 mg l^{-1} 2-nitrophenol into the carrier stream.

3.3. Interferences

Several chloro- and nitrophenols were tested to assess their influence on 2-nitrophenol signals. Solutions containing an interferent: 2-nitrophenol mass ratio of 5 : 1 were used for 1 mg l^{-1} of 2-nitrophenol. Results are shown in Table 1.

It was observed that none of the chlorophenols tested interfered with the signal for 2-nitrophenol (deviations below 2%); chlorophenols are easily oxidizable compounds, and in the experimental condi-

Table 1
Effect of inorganic and organic species on the determination of 1 mg l^{-1} 2-nitrophenol samples[a]

Interferent	Found (mg l^{-1})	ϵ (%)
Ni^{2+}	0.997	−0.3
Co^{2+}	0.997	−0.3
Cu^{2+}	2.295	+129
Cr^{3+}	0.997	−0.3
Pb^{2+}	1.971	+94
Al^{3+}	0.997	−0.3
Fe^{3+}	0.995	−0.5
Fe^{2+}	0.997	−0.3
NH_4^+	0.995	−0.5
Zn^{2+}	0.997	−0.3
Mn^{2+}	0.997	−0.3
NO_3^-	0.995	−0.5
SiO_3^{2-}	0.997	−0.3
CO_3^{2-}	0.995	−0.5
PO_4^{3-}	0.995	−0.5
Picric acid	1.099	+10
2,4-Dinitrophenol	1.147	+15
4-Nitrophenol	1.006	+0.6
2-Methyl-4,6-dinitrophenol	1.301	+30
2,4,6-Trichlorophenol	0.982	−1.8
Pentachlorophenol	0.982	−1.8
2,4-Dichlorophenol	0.985	−1.5
4-Chloro-3-methylphenol	1.006	+0.6

[a] For interferent: 2-nitrophenol at a mass ratio of 5 : 1.

tions used, these were either not active or gave small signals which did not cause high deviations.

All the nitrophenols, with the exception of 4-nitrophenol, were found to interfere. For 4-nitrophenol, the analyte can be selectively detected due to a more negative peak potential for the interferent (−1.0 V for 4-nitrophenol). Picric acid, 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol produce two peaks; for these compounds the peak potentials for the second peaks were very near to the peak potential for 2-nitrophenol, and high deviations are observed.

The possible interference of inorganic species was also tested. A great number of species showed no effect on 2-nitrophenol signals, with deviations below 1%. Only Pb^{2+} and Cu^{2+} were found to interfere; both species show cathodic peak potentials and high peak heights.

The proposed method has been applied to the direct determination of 2-nitrophenol in sea water spiked with 2-nitrophenol. The samples injected did contain 0.5, 1.0 and 2.5 mg l^{-1}, and recoveries of 106%, 97% and 94% were obtained, respectively. The samples were also tested by LC with ultraviolet detection (EPA Method no. 604); the analysis was carried out by the Central Service of Science and Technology of the University of Cádiz. No signal for 2-nitrophenol was observed when the sea water samples were analyzed. The concentration of the spiked samples tested were the same as obtained previously: 0.5, 1 and 2.5 mg l^{-1}. Recoveries of 100.1, 97.1 and 100.5 were obtained, respectively.

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