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Electrochemical determination of carbaryl oxidation in natural water and soil samples

J.A. Pérez-López, A. Zapardiel, E. Bermejo, E. Arauzo, L. Hernández

Department of Analytical Chemistry and Instrumental Analysis, Autonoma University, E-28049 Madrid, Spain

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Abstract. An electrochemical method for the determination of carbaryl, after prior oxidation to 1,4-naphthoquinone in natural water and soils is reported. The coulometric oxidation of carbaryl at a platinum electrode was studied using 0.024 mol/L Britton-Robinson buffer (pH 7.0). The reduction of the oxidation product 1,4-naphthoquinone at a dropping mercury electrode was used for the indirect determination of carbaryl after separation on C_{18} Sep-pak cartridges by differential pulse polarography (detection limits: 0.41 mg L^{-1} of water and 0.47 mg kg^{-1} of soil) and directly without separation by adsorptive stripping voltammetry (detection limits: 5 μg L^{-1} of water and 7 μg kg^{-1} of soil, for 75 s preconcentration time). Relative errors were lower than 3.7% and relative standard deviations smaller than 4.5%.

Introduction

1-Naphthylmethyl carbamate, commonly known as carbaryl or sevin® is a contact and stomach carbamate insecticide recommended for use at 0.25–2.0 kg/ha against many insects of cotton, fruit, vegetables and other crops. There is no evidence of phytotoxicity at theses rates. For rats, the acute oral LD_{50} is 850 mg/kg and percutaneous LD_{50} is 4000 mg/kg [1, 2].

Carbaryl is one of the least toxic of the carbamate pesticides in spite of its great insecticide capacity. Oxidations are the principal routes of initial metabolism of carbaryl [1, 2].

For the analytical determination of carbaryl mainly gas chromatography [3–6] and HPLC [7–11], and marginally thin-layer chromatography [3, 12, 13] have been used. The spectrophotometric methods used are generally based on the hydrolysis of carbaryl to 1-naphthol [14, 15] or on the formation of coloured complexes [16–20]. Carbaryl determinations using mass spectrometry [21, 22] and spectrofluorometry [9, 23–25] have also been carried out. Carbaryl is not polarographically active, it only gives a characteristic reduction wave after nitrosation [26, 27].

Correspondence to: J.A. Pérez-López

The electrode process of the 1,4-naphthoquinone reduction at the dropping mercury electrode has been studied [28–30]. These studies showed that 1,4-naphthoquinone presents a quasi-irreversible cathodic wave in acid and neutral media.

Adsorptive stripping voltammetry (AdSV) is regarded as a highly sensitive electrochemical technique suitable for the determination of low concentrations. Our laboratories have carried out determinations of several compounds using interfacial accumulation as an effective preconcentration step prior to voltammetric measurements [31–33].

The increasing use of carbamate insecticides in agriculture demands the development of highly sensitive and selective methods to determine low level residues of these compounds in complex matrices. Because the methods found in literature (mostly chromatographic) usually require several stages and chemical reactions that have to be accurately controlled to obtain reproducible responses, and because of the scarce development of electrochemical methods for the determination of carbaryl (as it is not electroactive at the mercury electrode), its determination via its coulometric oxidation product 1,4-naphthoquinone has been studied. The latter can be determined by differential pulse polarography and adsorptive stripping voltammetry, which allow the determination of the pesticide at trace level in natural water and soil.

Experimental

Apparatus and reagents

All differential pulse polarographic and adsorptive stripping voltammetric experiments were performed using a Metrohm 646 VA processor in conjunction with a 647 VA stand. A three-electrode system was used, made up of a Ag/AgCl/3 mol/L KCl reference electrode, a glassy carbon auxiliary electrode and a multimode dropping mercury electrode (Metrohm 6.1246.020). The latter served as the working electrode in the stationary MDE mode for the studies in differential pulse polarography and in the hanging mode (HMDE) with a surface of 0.60 mm^2 for the studies in adsorptive stripping voltammetry.

For the coulometric study a Metrohm E524 coulometer was used. A platinum plate with an area of 9 cm^2 served as the working electrode. The platinum wire auxiliary electrode was isolated from the solution by a glass frit. The potentials were referred to the saturated calomel electrode. The solution was stirred by means of a magnetic stirrer.

Stock solutions of 1.0×10^{-2} and 1.0×10^{-3} mol/L of pure carbaryl (Energias e Industrias Aragonesas S.A.) and of 1,4-naphthoquinone were prepared by dissolving the compounds in methanol. The solutions were stored in the dark under refrigeration to minimise the risk of decomposition. Diluted aqueous solutions were daily prepared from the stock solutions.

Supporting electrolytes were Britton-Robinson, acetate, phosphate, carbonate and borate buffers, and sodium hydroxide in different concentrations. All aqueous solutions were prepared in purified water (Milli Q and Milli Ro-Millipore).

Natural water and soil samples were obtained from the countryside at Segovia.

Procedures

Coulometry. 150 mL of the carbaryl solution of variable concentration in 0.024 mol/L Britton-Robinson buffer (pH 7.0) were placed into the coulometric cell. A constant potential usually 1.40 V (vs. SCE) was applied. The oxidation time depends on the carbaryl concentration. The solution was continuously stirred during the electrolysis period.

Differential pulse polarography. The technique was applied to hydroalcoholic solutions of carbaryl (5% methanol). Unless otherwise specified, the following conditions were used: drop time 1 s, pulse amplitude 50 mV and scan rate 6 mV s^{-1}. Deoxygenation was accomplished by passing purified nitrogen (99.999%) through the cell during 10 min.

Adsorptive stripping voltammetry. 25.0 mL of the carbaryl solution in 0.10 mol/L sodium hydroxide were placed into the polarographic cell and deoxygenated with nitrogen (99.999%) for 5 min in the initial cycle and then for 30 s in each successive cycle. The accumulation potential (usually -0.25 V) was applied to a fresh drop of mercury, the solution being stirred throughout the accumulation period. Stirring was stopped and the solution was given a 5 s rest time, after which a differential pulse scan (pulse amplitude 50 mV and scan rate 20 mV s^{-1}) was initiated towards more negative potential values.

Carbaryl determination as 1,4-naphthoquinone in natural water and soils by differential pulse polarography

Natural waters. A Waters Associates C_{18} Sep-pak cartridge was activated with 5 mL of methanol and rinsed twice with 3 mL of distilled water. The cartridge was then buffered at pH 7.0 with 2 mL of 0.04 mol/L Britton-Robinson buffer (pH 7.0), after which carbaryl was separated by passing 25.0 mL of natural water (containing 1.80–4.40 mg of carbaryl per litre of water) through the cartridge, where the pesticide was retained. The cartridge was washed with 5 mL of distilled water. Carbaryl was eluted with four 2 mL portions of a mixture of diethyl ether and n-hexane (1:1) and the combined eluent was evaporated with a stream of nitrogen. The resulting residue was dissolved in 1 mL of methanol and diluted to 150 mL with 0.024 mol/L Britton-Robinson buffer of pH 7.0. The solution thus obtained was ready for coulometric oxidation. After the electrolysis, 10.0 mL were diluted with 10.0 mL of 0.10 mol/L sodium hydroxide and the corresponding differential pulse polarograms were recorded (drop time 1 s, pulse amplitude 50 mV and scan rate 6 mV s^{-1}).

Soils. The soil sample (containing 1.80–24.40 mg of carbaryl per kg of soil) was consecutively passed through two sieves of 2 mm and 1 mm diameter. Next, 25.0 g of the soil sample were mixed and shaken with 25.0 mL of distilled water during 30 min to ensure total mixing of soil components. The suspension was filtered by suction through a Büchner funnel. The filtrate was analysed according to the above procedure for water.

Direct determination of carbaryl as 1,4-naphthoquinone in natural water and soils by adsorptive stripping voltammetry

Natural waters. A 25.0 mL sample of natural water (containing 0.024–0.244 mg of carbaryl per litre) was diluted to 150 mL with 0.024 mol/L Britton-Robinson buffer (pH 7.0). After the coulometric oxidation at 1.40 V (vs. SCE) constant potential, 10.0 mL of the solution were diluted with 10.0 mL of 0.10 mol/L sodium hydroxide. The solution thus obtained was ready for analysis by adsorptive stripping voltammetry (75 s of accumulation at -0.25 V).

Soils. The above procedure for soils was then used on soils containing 0.024–0.244 mg of carbaryl per kg of soil. The filtrate obtained was subjected to the above procedure for water with analytical measurement by adsorptive stripping voltammetry.

Results and discussion

Coulometric study of the carbaryl oxidation

For studying the coulometric oxidation the ultraviolet spectra and differential pulse polarograms were recorded for different oxidation times. Figure 1 shows the evolution of the absorption spectra during the electrolysis. For 0 min oxidation time there was only an absorption maximum at 278 nm, which corresponds to carbaryl. During oxidation this maximum diminished and a new maximum appeared at 245 nm, whose absorbance increased with the electrolysis time. The absorbance of the new maximum,

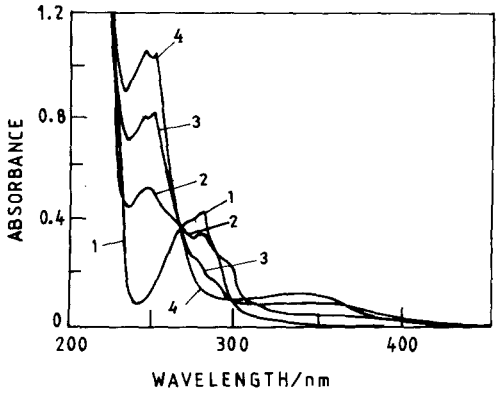

Fig. 1. Evolution of the UV spectrum during the coulometric oxidation of carbaryl. Coulometer carbaryl concentration 1.0×10^{-4} mol/L. Oxidation potential 1.40 V. Oxidation times: 0(*1*), 180(*2*), 360(*3*), 540(*4*) min

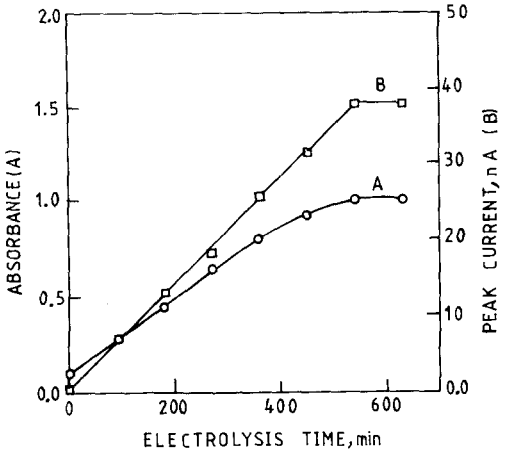

Fig. 2. Influence of the electrolysis time on the absorbance and the peak current. (*A*) absorbance at 245 nm; (*B*) peak current at −0.68 V. Conditions as in Figs. 1 and 3

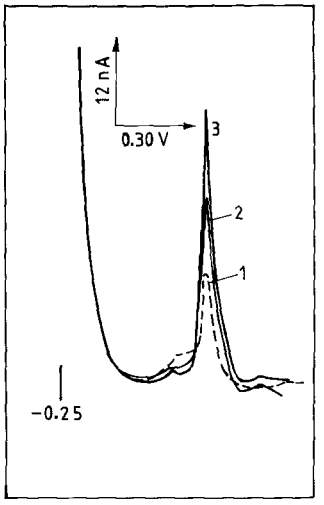

Fig. 3. Evolution of the differential pulse polarograms during the coulometric oxidation of carbaryl. Oxidation times: 180(*1*), 360(*2*), 540(*3*) min. Differential pulse polarography in 0.10 mol/L sodium hydroxide as electrolyte: 1 s drop time, 50 mV pulse amplitude and 6 mV s^{-1} scan rate. Other conditions as in Fig. 1

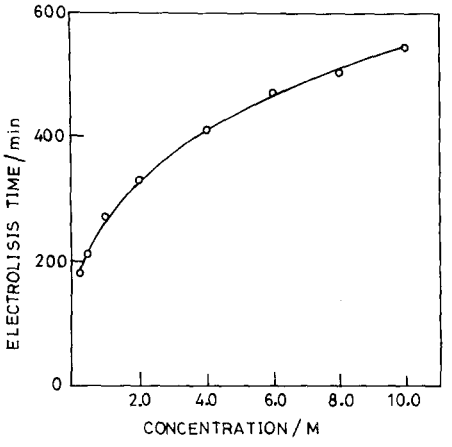

Fig. 4. Influence of the carbaryl concentration on the time of the complete oxidation. Concentrations and conditions as in Figs. 1 and 3

corresponding to the oxidation compound, reached the maximum at an oxidation time of 540 min, then it remained constant (Fig. 2A), indicating that the carbaryl oxidation had been completed.

Similar results were observed with differential pulse polarography (Fig. 3). Carbaryl is not electroactive at the dropping mercury electrode. In the course of the coulometry a polarographic peak was obtained corresponding to the reduction of the oxidation product at the electrode (peak potential −0.68 V). The peak current increased with the oxidation time up to 540 min, after which it remained constant (Fig. 2B). The results obtained confirmed that the oxidation was completed after 540 min. The coulometric experiments proved that the complete oxidation time depends on the concentration (Fig. 4).

The oxidation compound was identified as 1,4-naphthoquinone by thin-layer chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy. The results obtained with these techniques for the carbaryl oxidation product and pure 1,4-naphthoquinone were identical. By comparing the differential pulse polarograms and ultraviolet absorption spectra of the oxidation product with those obtained with pure 1,4-naphthoquinone, an average of the transformation of 96% was calculated.

Study of 1,4-naphthoquinone by differential pulse polarography

The differential pulse polarograms obtained for 1,4 naphthoquinone solutions at different concentrations and with various supporting electrolytes show a very well defined reduction peak. The best results were observed for pH 6.0 in 0.04 mol/L Britton-Robinson buffer (peak potential −0.30 V) and for 0.10 mol/L sodium hydroxide (peak potential −0.68 V) (Fig. 5). It was observed that a

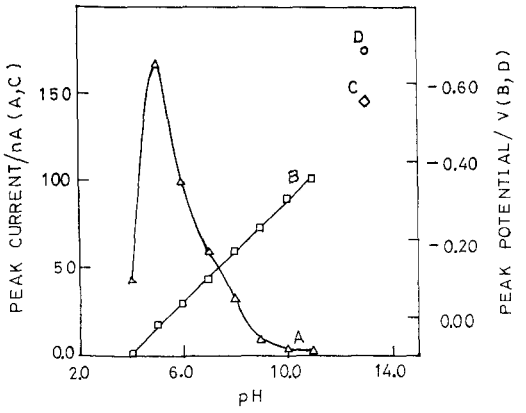

Fig. 5. Influence of the pH on the peak current and the peak potential for 1.0×10^{-5} mol/L naphthoquinone. Electrolytes: 0.04 mol/L Britton-Robinson buffer (*A*, *B*) and 0.10 mol/L sodium hydroxide (*C*, *D*). Differential pulse polarography conditions as in Fig. 3

progressive increase in methanol percentage of the solutions produces a decrease in the polarographic signal for percentages greater than 10%; 5% of methanol was chosen for the study.

In the study of the influence of instrumental parameters, optimum values were obtained with a 1 s drop time, a 50 mV pulse amplitude and a 4 mV s^{-1} scan rate. With 0.04 mol/L Britton-Robinson buffer (pH 6.0) and 0.10 mol/L sodium hydroxide, the peak current was observed to vary linearly with the 1,4-naphthoquinone concentration. The best sensitivity was obtained in 0.10 mol/L sodium hydroxide; the peak current depends on the concentration according to the equation: $Ip/nA = 2.01 + 1.54 \times 10^7 C/M$, $r = 0.9991$ ($n = 11$); the concentration range is $5.0 \times 10^{-7} - 1.0 \times 10^{-5}$ mol/L.

The detection limit (3σ) obtained is 1.7×10^{-7} mol/L and the determination limits (10σ) 5.2×10^{-7} mol/L. The mean relative error for 1,4-naphthoquinone determination was lower than 2.0% and the relative standard deviation was less than 2.8% for a series of seven solutions with different concentrations ranging from 5.0×10^{-7} to 1.0×10^{-5} mol/L.

Study of 1,4-naphthoquinone by adsorptive stripping voltammetry

1,4-Naphthoquinone adsorption on the HMDE surface at pH 12–13 was observed by comparing voltammograms obtained after 60 s of accumulation time for −0.25 V with those recorded without accumulation. The voltammograms obtained with accumulation exhibited higher peaks than the non-accumulation records under similar conditions. The highest current values were obtained in 0.10 mol/L sodium hydroxide (see Fig. 6). In this electrolyte, for 1.0×10^{-7} mol/L 1,4-naphthoquinone, the 60 s accumulation experiment yielded a peak current 3.6-fold higher than without accumulation; so this electrolyte was selected to develop the method for the determination of 1,4-naphthoquinone.

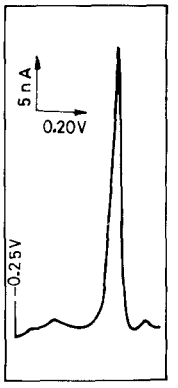

Fig. 6. Adsorptive stripping voltammetry for 1.0×10^{-7} mol/L naphthoquinone in 0.10 mol/L sodium hydroxide. Conditions: −0.25 V accumulation potential, 100 s accumulation time, 5 s rest time, 0.60 mm^2 drop size, 50 mV pulse amplitude, 20 mV s^{-1} scan rate and 1,920 rpm stirring speed

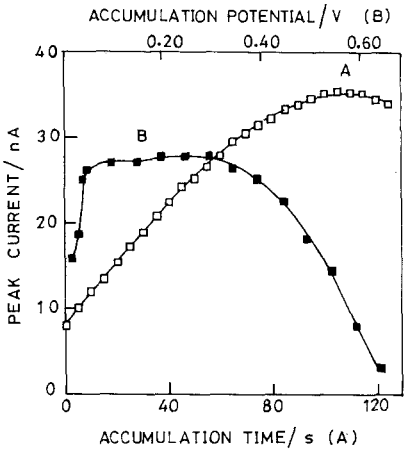

Fig. 7. Variation of peak current with accumulation potential (*A*) and accumulation time (*B*) in adsorptive stripping voltammograms of naphthoquinone in 0.10 mol/L sodium hydroxide. Conditions as in Fig. 6

The influence of the accumulation potential (between 0.00 and −0.65 V) on the stripping peak current was studied. The response was found to be higher for accumulation potentials between −0.10 and −0.30 V (Fig. 7). A −0.25 V accumulation potential was therefore adopted.

The dependence of the stripping peak current on accumulation time was linear up to 50 s (Fig. 7), with a slope of 0.24 nA s^{-1}, and a correlation coefficient of 0.9991 ($n = 10$). The selection of the optimum accumulation time depends on the concentration range to be studied. For 1.0×10^{-7} mol/L a 100 s accumulation time was chosen.

The drop size and the instrumental parameters affect the voltammetric response; the best conditions were obtained with 0.60 mm^2 drop size (maximum allowed by the equipment used), 50 mV pulse amplitude, 20 mV s^{-1} scan rate and 1920 rpm stirring rate. Rest times between 0 and 50 s have no influence on the voltammograms obtained. A rest time of 5 s was therefore chosen.

The influence of the 1,4-naphthoquinone concentration was studied under the optimum conditions at various accumulation times. The calibration graphs obtained show that the response is linear for the concentration range studied ($5.0 \times 10^{-9} - 1.0 \times 10^{-7}$ mol/L) with sensitivities of 2.62×10^8 nA mol^{-1} L (50 s, $r = 0.9990$) and

3.48×10^8 nA mol^{-1} L (100 s, r = 0.9995). For 100 s accumulation time, a detection limit (3σ) of 0.9×10^{-9} mol/L and a determination limit (10σ) of 3.0×10^{-9} mol/L were calculated. The reproducibility was then studied for 100 s, giving a relative standard deviation of 3.8%. For 4.0×10^{-8} mol/L 1,4-naphthoquinone, a mean relative error lower than 2.9% was calculated.

Carbaryl determination as 1,4-naphthoquinone in natural water and soils

Differential pulse polarography. The analytical procedure described in the Experimental section was applied for the determination of carbaryl in natural water and soils, previous separation of interfering substances with C_{18} cartridges and later coulometric oxidation to 1,4-naphthoquinone, since the peak current is directly dependent on the concentration. Different eluents were used in the separation study; the best results were obtained with dichloromethane (82% recovery) and diethyl ether/n-hexane (1:1) mixture (90% recovery).

Table 1 summarises the results obtained. In the concentration range of linear response the mean relative errors are less than 2.7%. The method is quite reproducible and the precision (expressed in terms of relative standard deviation) is 3.3% for 10 mg carbaryl L^{-1} natural water (n = 10) and 3.9% for 10 mg carbaryl kg^{-1} soil (n = 10). The standard addition method could also be used in the carbaryl range in which the response is linear.

Adsorptive stripping voltammetry. Natural water and soil samples with different carbaryl amounts were tested following the procedure described in the Experimental section. The voltammetric peaks were well defined and similar to those observed in the study on distilled water.

Table 1. Results obtained in the determination of carbaryl in natural water and soils by differential pulse polarography; previous separation with C_{18} sep-pak cartridges and oxidation to 1,4-naphthoquinone

	Natural waters	Soils
Linear response	1.81–24.14 mg L^{-1}	1.81–24.14 mg Kg^{-1}
Sensitivity	4.67 nA mg^{-1} L	2.86 nA mg^{-1} Kg
Correlation coefficient	0.998	0.997
Determination limit	1.23 mg L^{-1}	1.42 mg Kg^{-1}
Detection limit	0.41 mg L^{-1}	0.47 mg Kg^{-1}

Table 2. Results obtained in the determination of carbaryl in natural water and soils by adsorptive stripping voltammetry; previous oxidation to 1,4-naphthoquinone

	Natural waters	Soils
Linear response	0.244–0.024 mg L^{-1}	0.244–0.024 mg Kg^{-1}
Sensitivity	72.05 nA mg^{-1} L	39.95 nA mg^{-1} Kg
Correlation coefficient	0.9992	0.998
Determination limit	0.016 mg L^{-1}	0.020 mg Kg^{-1}
Detection limit	0.005 mg L^{-1}	0.007 mg Kg^{-1}

The results obtained prove that direct determination of carbaryl in natural water and soils is possible.

Calibration plots were obtained at different preconcentration times, with –0.25 V accumulation potential. The best sensitivity values were obtained for an accumulation time of 75 s. Table 2 summarises the results obtained for natural water and soils by adsorptive stripping voltammetry. When analysing a series of five solutions of carbaryl in amounts of 0.024–0.244 mg L^{-1} of natural water and 0.024–0.244 mg kg^{-1} of soil (75 s accumulation time), the relative error was found to be less than 3.7% and the mean standard deviation lower than 4.5%.

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