

## VOLTAMMETRIC STUDY WITH A GLASSY CARBON ELECTRODE OF THE PESTICIDES FENTHION AND FENITROTHION

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### SUMMARY

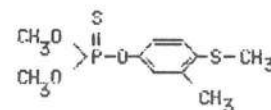
The voltammetric behaviour (d.c. and d.p.v.) of the pesticides Fenthion and Fenitrothion on a glassy carbon electrode is described. Fenthion is oxidized at + 1.20 V (vs Ag/AgCl) but Fenitrothion is reduced at - 0.60 V. Both electroanalytical responses can be used for the determination of the two pesticides with detection limits of 1.36 and 0.46  $\mu$ M, respectively.

KEYWORDS : d.c. and d.p. voltammetry, pesticides, Fenthion, Fenitrothion, glassy carbon, electrode treatment.

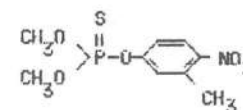
### INTRODUCTION

Methods for the determination of pesticides are of evident interest; most of them are spectrophotometric or chromatographic but electrochemical determination is becoming more and more used (1,2). Initially, the mercury drop electrode was employed as the working electrode; however it has been gradually replaced by solid electrodes. Among these, glassy carbon has been most used (3).

In the present work an electroanalytical study was carried out the pesticides Fenthion (3-methyl-4-methylthiophenyl dimethyl phosphothionate), and Fenitrothion (3-methyl-4 nitrophenyl dimethyl phosphothionate). The study was performed using conventional and differential pulse voltammetry, both with a rotatory glassy carbon electrode.



Fenthion



Fenitrothion

These pesticides are highly soluble in organic solvents but fairly insoluble in water. Fenthion is quite resistant to acid and alkaline hydrolysis while Fenitrothion is readily hydrolyzable in alkaline media.

## EXPERIMENTAL

### Apparatus and Reagents.

A METROHM E-506 polarograph was employed coupled with a METROHM 628-10 power source and a METROHM-628-50 electrode holder motor with a glassy carbon working electrode METROHM EA-289/1GC, a METROHM EA-441-5 Ag/AgCl reference electrode, and a METROHM EA-285 platinum auxiliary electrode. Statistical treatment was carried out with the "Statwork" program for an Apple Macintosh computer.

Methanolic solutions of the pesticides were prepared from the products in liquid form: Fenthion (Bayer, 98.5% purity) and Fenitrothion (Zeltia Agraria, 96% purity). Acetic acid, sodium acetate, sodium hydroxide and Britton-Robinson buffer solution were prepared from the corresponding reagent grade products.

### Procedure.

When the electrode is employed in anodic processes a polish with alumina and treatment in two steps are recommended. The first of these is a **preconditioning** in solutions of supporting electrolyte and application of a constant potential of +1.4 V for three minutes or carrying out several successive anodic sweeps. The second comprises **pretreatment** and involves application of a constant potential of -1.2 V followed by another of +1.4 V for 30 sec each in solutions containing pesticide.

In cathodic processes, the preconditioning step is carried out by applying a constant potential of -1.2 V for 5 min or performing several cathodic sweeps in a deaerated supporting solution.

The studies were conducted in the presence of 0.06M HAc, 0.04 M NaAc as supporting electrolyte in 20% (v/v) MeOH/H<sub>2</sub>O. For the study of the influence of the pH 0.12 M Britton-Robinson buffer was used as the supporting electrolyte. After bubbling nitrogen through the solutions for 10 min, when necessary, the corresponding voltammograms were recorded. The potential sweeps were made from -0.2 to 1.2 V, with a sweep rate of potentials of 8 mV/s and a rotation rate of the electrode of 1500 r.p.m. for

the solutions of Fenthion and from 0.6 to 1.4 V with rates of 5 mV/s and 1540 r.p.m., respectively, for the Fenitrothion.

## RESULTS AND DISCUSSION

### 1. Treatment of electrode

To study the behaviour of the glassy carbon electrode the I-V curves of solutions of each of the pesticides were recorded by DPV after subjecting the electrode to different treatments. Having found the most suitable treatment, the corresponding voltammograms were also recorded by the conventional technique. The influence of treatment of the solid electrodes on the voltammetric response is of such importance that its study constitutes a common denominator of all the works related to this field (4).

The so-called "preconditioning" step, a term introduced by Blaedel and Jenkin (5) merits special consideration; it can be carried out at any moment of the lifetime of the electrode, but specially when it has not been used for some time.

For anodic processes and if in fact the electrode has been used in the zone of cathodic potentials, it is advisable to perform a preconditioning step consisting in placing the electrode in a solution of supporting electrolyte and making several successive anodic sweeps or applying a constant potential of 1.4 v for three minutes. Under these conditions, voltammograms of background solution with small residual currents and without peaks owing to the electrochemical oxidation of functional groups on the surface of the electrode are obtained. In this way the electrode can be used over several days.

For cathodic processes the situation is slightly different: when successive sweeps are performed a reduction wave appears owing to the reduction of oxidized species (from the solution and the electrode) formed on the surface of the electrode. This wave appears whenever the electrode has been previously held at very anodic potentials. On successive cathodic sweeps a decrease occurs in the reduction current and a shift towards less cathodic potentials of the reduction of the medium. After 8 or 10 sweeps, or when applying a constant potential of -1.2 v for 5 min, the reduction wave disappears (Figure 1 A). Identical behaviour is observed when the electrode has been exposed to atmospheric oxygen or when the electrode, after polishing, drying and preconditioning is allowed to stand in deaerated

background solution for 24 hours. The first sweep of potentials shows a reduction peak that in later sweeps disappears (Figure 1 B).

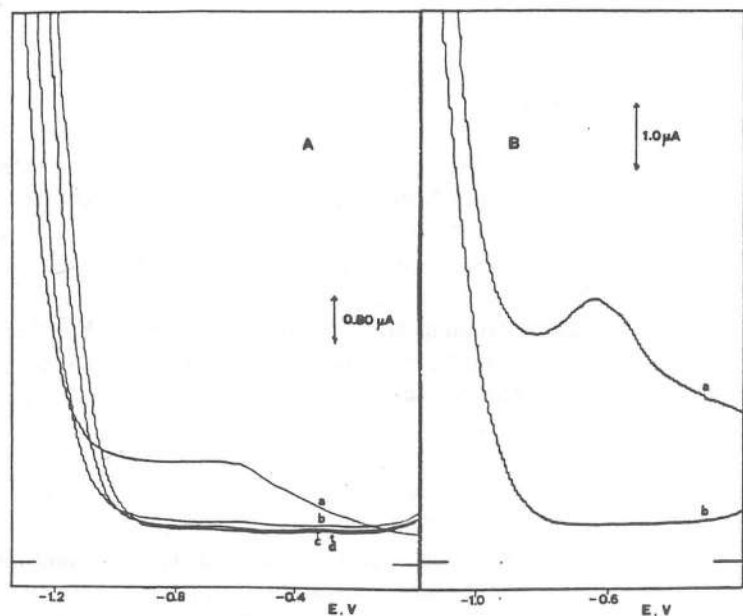


Figure 1. Cathodic voltammograms of background solution (DPV).  
 Freshly polished electrode.  
 HAc 0.06 M NaAc 0.04 M CH<sub>3</sub>OH 20 % (v/v)  
 A) Successive sweeps : a) 1<sup>o</sup> b) 2<sup>o</sup> c) 3<sup>o</sup> d) 8<sup>o</sup>  
 B) At 24 hours : a) Initial sweep b) Electrode at -1.2 V over 5 min.

Since it is impossible to avoid the formation of these reducible species on the surface of the electrode, it is recommended to perform the cathodic preconditioning step daily by applying a constant potential of -1.2 V for 5 min or several cathodic sweeps on a deaerated supporting solution.

The results obtained (Figure 2) on several successive sweeps after cathodic preconditioning clearly show that this does not lead to a reducible surface, rather it simply cleans the surface of reducible species such that for to activate the electrode it is necessary to perform a pretreatment.

Figure 2 shows the variation in peak currents obtained as a function of the number of sweeps carried out in both zones of potential with the electrode recently polished and preconditioned. For anodic processes a decrease in the response with the number of sweeps carried out is observed (Figure 2); reaching almost constant values when the number of sweeps is greater than 10.

For cathodic processes (Figure 2) the behaviour is similar, observing a decrease in the peak current with the number of sweeps made and with a constancy in the values for a similar number of sweeps.

In both cases, similar responses are produced if the electrode is held at a suitable potential (+1.4 or -1.2 V) for five minutes.

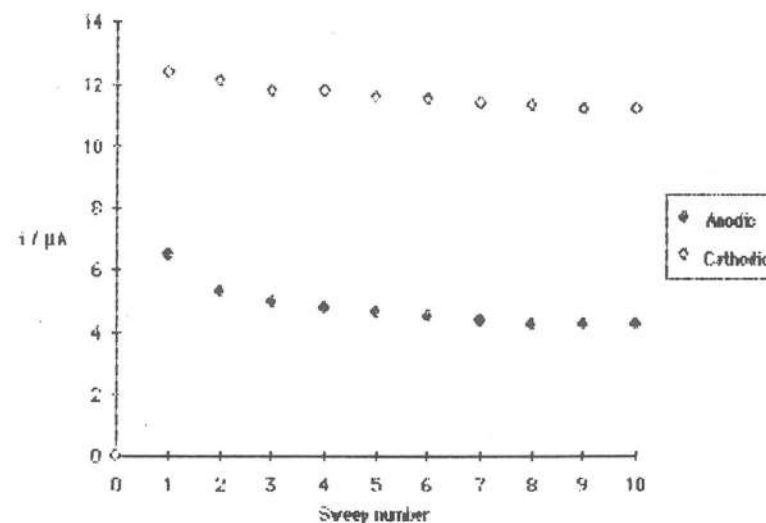


Figure 2. Variation of peak currents with the number of sweeps.  
 [Fenthion] :  $5.50 \cdot 10^{-5}$  M. [Fenitrothion] :  $6.40 \cdot 10^{-5}$  M

To optimize the stability of the voltammetric response several experiments were performed. A polishing of the electrode before each measurement leads to results that are not easy to reproduce. We also