

## Voltammetric determination of malathion

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The cathodic adsorptive stripping differential pulse voltammetric method was proposed for the determination of malathion {S-bis (etoxy carbonyl) ethyl O,O-dimethyl phosphorodithioate}. The voltammetric response was evaluated in 0,04 mol l<sup>-1</sup> Britton-Robinson buffer with respect to the accumulation time and potential, and concentration dependence. The relationship between peak current and malathion concentration was linear within the range of  $1 \times 10^{-7}$  –  $8 \times 10^{-7}$  mol l<sup>-1</sup>. Interferences from some other organophosphorus insecticides on the determination of malathion were studied.

Keywords: voltammetry, malathion, organophosphorus insecticides.

### 1. INTRODUCTION

Organophosphorus compounds form one of the most important classes of insecticides. They are effective against a wide range of insects on fruits, vegetables and commercial crops. Reliable analytical procedures are therefore needed for their determination. Spectrophotometric, GC, HPLC and electrochemical techniques have been used for determination of a number of organophosphorus pesticides [1-15].

In the present paper the determination of malathion {S-bis (etoxy carbonyl) ethyl O,O-dimethyl phosphorodithioate} by adsorptive stripping differential pulse voltammetry and interferences from some other organophosphorus insecticides on the determination of malathion are discussed.

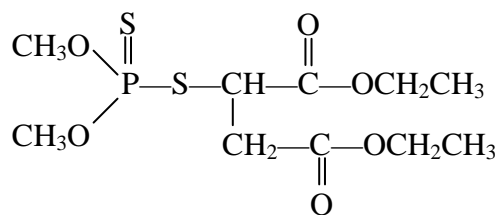


Fig.1. Structure of the pesticide malathion

## 2. EXPERIMENTAL

A PA-4 polarograph with a Model 4106 X-Y recorder (Laboratorni Pristroje, Prague) was used, with an SMDE-1 hanging mercury drop electrode (HMDE) (Laboratorni Pristroje), a platinum auxiliary electrode and an Ag/AgCl reference electrode.

Malathion, fenitrothion, dimethoat, chlorfenvinphos, chlorpyrifos and chlorpyrifos methyl (Institute of Organic Chemical, Warsaw) stock solutions ( $1 \times 10^{-3} \text{ mol l}^{-1}$ ) were prepared by dissolving an appropriate amount of compound in methanol. All insecticides were analytical grade.

Britton-Robinson buffer was prepared from an appropriate amount of o-phosphoric acid (85%, Fluka, for trace analysis), boric acid (Merck, suprapur), sodium hydroxide monohydrate (Merck, suprapur) and acetic acid (Merck, suprapur). Thrice distilled water was obtained from a Heraeus apparatus.

The test solution was placed in a polarographic cell and deoxygenated by passing purified nitrogen for 10 min. The voltammetric response was obtained using an amplitude of 50 mV and a scan rate of  $20 \text{ mV s}^{-1}$ .

## 3. RESULTS AND DISCUSSION

A Britton-Robinson buffer with different pH values was used as supporting electrolyte. The effect of the pH on the malathion stripping peak was tested (Fig. 2).

Malathion peak current  $I_p$  was observed with pH from 4.0 to 9.5. The peak potential is  $E_p = -1.03 \text{ V}$  and does not change with pH. Peak current of malathion is slowly increasing with pH. Max value of the peak current was obtained about pH 8.5, then slow decreasing of peak current was observed. Britton-Robinson buffer with pH about 7.0 was chosen for further investigation as the most promising from the analytical point of view.

The sensitivity of adsorptive stripping voltammetry depends on the accumulation time and accumulation potential. A series of accumulation potentials between -0.2 and -0.9 V were studied. Fig.3 shows, that the peak current varied very slightly with accumulation potential ( $E_{acc}$ ) between -0.2 and -0.7 V. For determination of malathion the optimal accumulation potential  $E_{ac} = -0.6$  V was chosen.

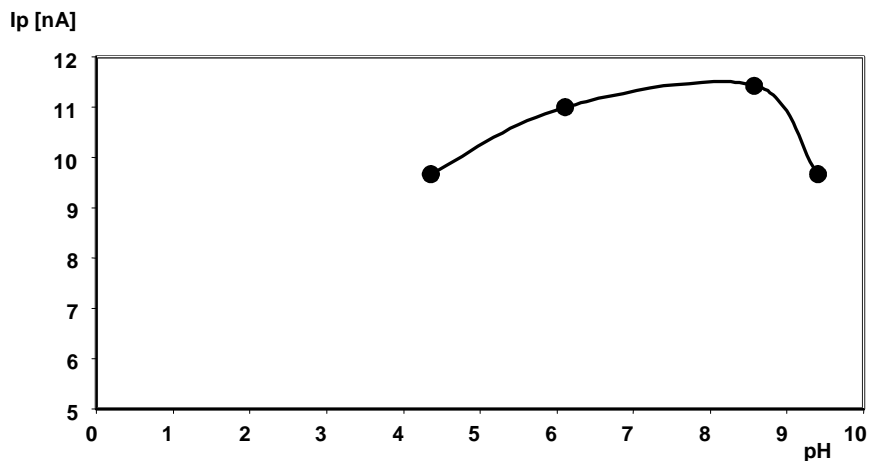


Fig. 2. Effect of pH on peak current of malathion. Concentration of malathion:  $20 \times 10^{-7}$  mol  $l^{-1}$ , without accumulation

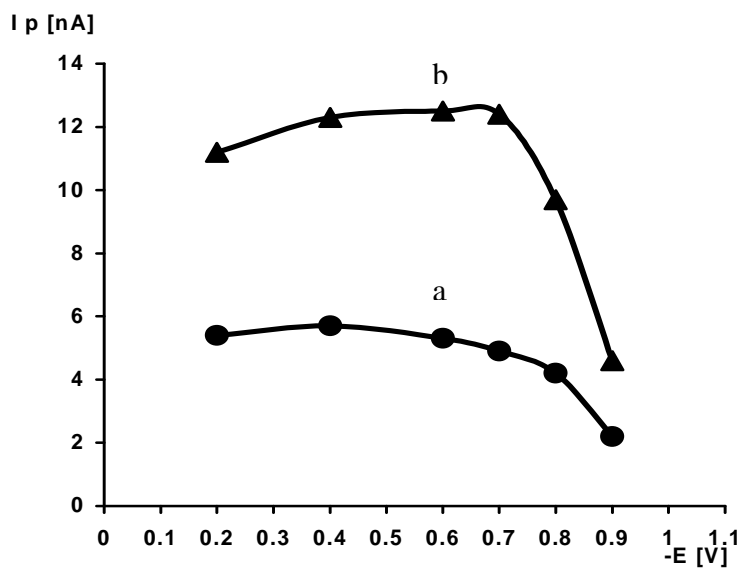


Fig. 3. Effect of accumulation potential on peak current of malathion. Concentration of malathion:  $5 \times 10^{-7}$  (a) and  $10 \times 10^{-7}$  (b) mol  $l^{-1}$ ; accumulation time: 30 s

Figure 4 shows that for  $5 \times 10^{-7} \text{ mol l}^{-1}$  of malathion strongly increasing peak current response is observed from 15 to 45 seconds accumulation, then the peak current increases slowly reaching maximum at  $t_{ac}=105$  seconds. Above  $t_{ac}=30$  seconds the peak currents are not repetitive.

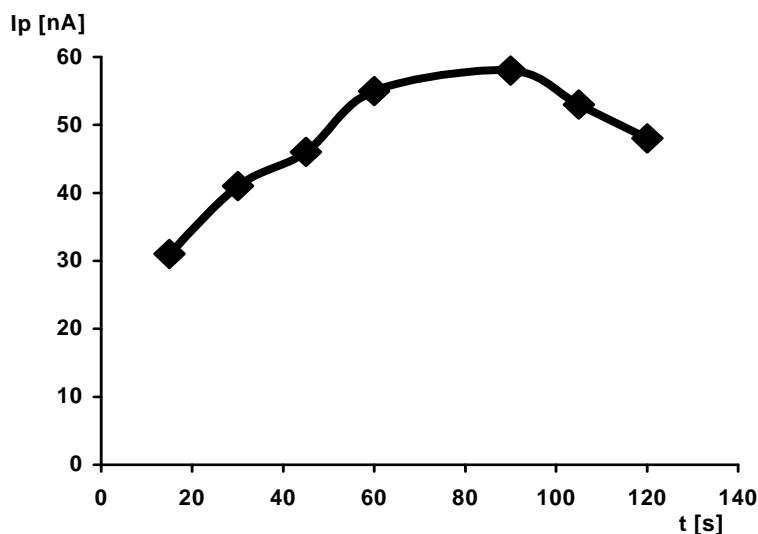
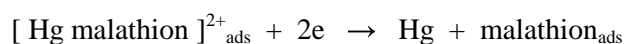
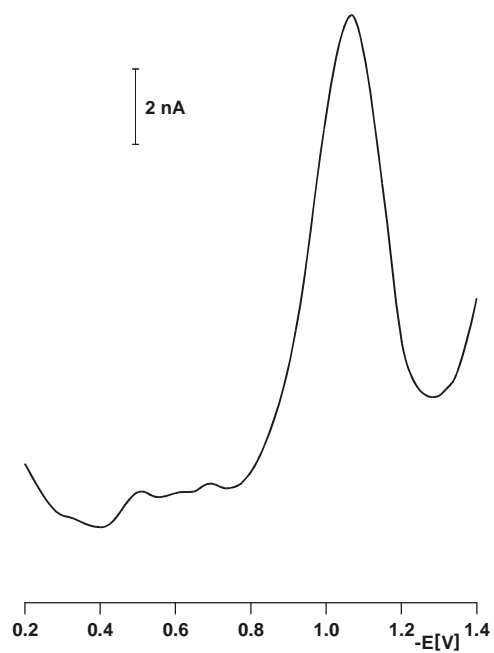


Fig. 4. Effect of accumulation time on peak current of malathion. Concentration of malathion:  $5 \times 10^{-7} \text{ mol l}^{-1}$ ; accumulation potential:  $-0.60 \text{ V}$

Figure 5 shows the representative differential pulse peak (a) and cyclic voltammogram (b) of malathion. Maybe the peak of malathion is attributed to the  $\text{Hg(II)}$  in the mercuric malathion complex. This compound was initially formed at the electrode surface via the interaction of the sulfur atom in the malathion compound with the charged mercury electrode surface. The interaction of the  $\text{P}=\text{S}$  group with the mercury electrode surface is not strongly. Thus, according to well known general mechanisms of the adsorptive voltammetric behaviour of many sulfur containing compounds [16-18] at the mercury electrode, the electrochemical reduction process could be presented by the following reaction:



a)



b)

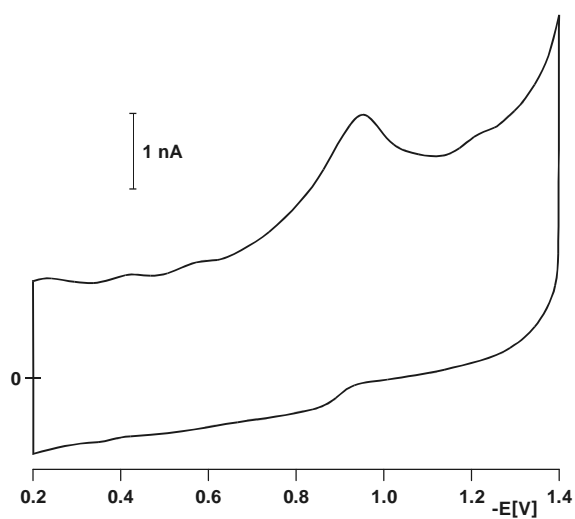


Fig. 5. Cathodic (a) and cyclic voltammogram (b) of malathion. Concentration of malathion:  $10 \times 10^{-7}$  (a) and  $20 \times 10^{-7}$  (b)  $\text{mol l}^{-1}$ ; accumulation time: 30 (a) and 0 (b) s.

The calibration graph for an accumulation time of 15 seconds was linear in the range from  $1 \times 10^{-7}$  to  $17 \times 10^{-7} \text{ mol l}^{-1}$  and obeyed the equation  $y=4.578x+1.0809$ , where  $y$  and  $x$  are the peak current (nA) and malathion concentration ( $\mu\text{mol l}^{-1}$ ), respectively. The calibration graph for an accumulation time of 30 seconds was linear in the range from  $1 \times 10^{-7}$  to  $8 \times 10^{-7} \text{ mol l}^{-1}$  and obeyed the equation  $y=7.336x+1.7591$ .

A possible interference with malathion determination from the following organophosphorous insecticides: fenitrothion, chlorfenvinphos, chlorpyrifos, chlorpyrifos methyl and dimethoat was examined. Above mentioned insecticides caused lowering of the malathion peak. This effect was observed in the case of fenitrothion only in three-fold excess, because the peak potential of fenitrothion is  $E_p=-0.46 \text{ V}$ . Other above insecticides, including malathion, have the peak potential about  $-1.0 \text{ V}$ .

#### Acknowledgements

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#### 4. REFERENCES

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## CURRICULUM VITAE



**M. K. Pawlak** received a M.Sc. degree in Chemistry from Poznań University, Mat. Phys. Chem. Department in 1972 and started her assistant work at Poznań University of Technology in the Institute of Chemistry and Technical Electrochemistry. M. K. Pawlak received Ph.D. in chemical sciences from Poznań University of Technology in 1977. Her dissertation was entitled: "Effect of polyethylene glycols on the determination of metal ions by voltammetry with accumulation on HMDE". M. K. Pawlak independently and with others has written above 20 papers in the area of analytical determination of metal ions, surfactants and pesticides using polarography and voltammetry methods.