

Voltammetric Determination of Fenitrothion

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Abstract

The adsorptive stripping differential pulse voltammetric method was proposed for the determination of fenitrothion [O,O-dimethyl O-(4-nitro-m-tolyl)phosphorothioate]. The voltammetric response was evaluated in 0,04 mol l⁻¹ Britton-Robinson buffer with respect to the accumulation time and potential, and concentration dependence. The relationship between peak current and fenitrothion concentration was linear within the range of 1x10⁻⁸ – 1x10⁻⁶ mol l⁻¹. In spiked water the detection limit of fenitrothion, estimated from 3 times the standard deviation, was 36 ng l⁻¹. Interference from some other organophosphorus insecticides on the determination of fenitrothion were studied.

Keywords: voltammetry, fenitrothion, organophosphorus insecticides, water

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. Spectrofotometric, GC, HPLC and polarographic techniques have been used for determination of a number of organophosphorus pesticides [1-10]. Polarographic methods have been used for determination of parathion, chlorpyrifos, chlorfenvinphos, dicrotophos and crotoxyphos [11-13]. But no work has been reported dealing with polarographic determination of fenitrothion.

In the present paper the determination of fenitrothion [O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate] by adsorptive stripping differential pulse voltammetry and interferences from some other organophosphorus insecticides on the determination of fenitrothion are discussed. This method was used for determination of fenitrothion in spiked water.

The structure of fenitrothion is displayed in Fig. 1.

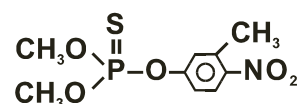


Fig.1. The structure of fenitrothion.

Materials and Methods

Apparatus

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

Reagents

Fenitrothion, dimethoat, malathion, chlorfenvinphos, chlorpyrifos and chlorpyrifos methyl (Institute of Organic Chemical, Warsaw) stock solutions (1x10⁻³ 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 hy-

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dioxide monohydrate (Merck, suprapur) and acetic acid (Merck, suprapur).

All organic solvents were freshly distilled in glass. Thrice distilled water was obtained from a Heraeus apparatus.

Voltammetric Measurements

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 mV s⁻¹.

Preparation and Extraction of Water Samples

1 l sample spiked with 138.6 ng of fenitrothion was passed through a column containing 1g of ODS (bonded silica C-18 used for the solid phase extraction). The column was first preconditioned with 5 ml of methanol and 2x5 ml of water. The sample was passed through the column at a flow rate of 10-15 ml min⁻¹. After the enrichment step the analyte was immediately eluted sequentially with 4 ml, then 1 ml, of ethylacetate. The solvent was evaporated to dryness. The residue was dissolved in 10 ml of 0.04 M Britton-Robinson buffer and its voltammogram was recorded. Determination of fenitrothion was performed using the multiple standard addition method.

Results and Discussion

A Britton-Robinson buffer with different pH values was used as supporting electrolyte. The effect of the

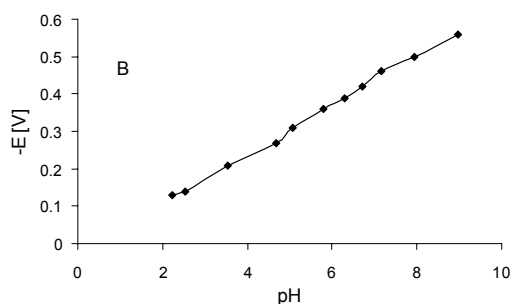
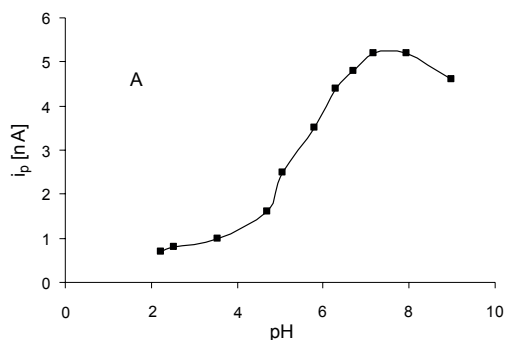


Fig.2. Effect of pH on peak current (A) and peak potential (B) of fenitrothion. Concentration of fenitrothion: 5×10^{-7} mol l⁻¹, accumulation potential: -0.20V, accumulation time: 30 s.

pH on the fenitrothion stripping peak was tested (Fig. 2). No fenitrothion peaks were observed at pH=1.8. At pH=4.5 one sharp peak at $E=-0.29$ V and two broad and lower ones at $E=-0.57$ V and $E=-1.02$ V were found. In the case of pH range of 6.5-7.5 there are two peaks of fenitrothion. The first sharp one appears at $E=-0.46$ V and the second, broad and low one, at $E=-0.97$ V. The sharp peak of fenitrothion appearing at $E=-0.46$ V in Britton-Robinson buffer with pH=7.0 was chosen for further investigation as the most promising from the analytical point of view. The other possible choice, the sharp peak found at pH=4.5, was not only lower than the chosen one but also more difficult to analyze due to its position ($E=-0.29$ V) resulting in enhanced influence of residual current. Other broad peaks were not suitable for analytical application.

Increasing values of the peak current i_p were observed with increasing pH up to 7.0. With pH>7 i_p values remained constant. This behavior seems to indicate more efficient adsorption of the deprotonated form of the fenitrothion. At pH 9.0 gradually decreasing i_p was observed.

In 0.04 M Britton-Robinson buffer, fenitrothion gives a linear relationship between peak potential E_p and pH. With increasing pH, the peak potential is shifted towards more negative values. This fact proves that it is the protonated form of fenitrothion which undergoes reduction [14-16]. The electrochemical reduction process could be presented by the following reaction:

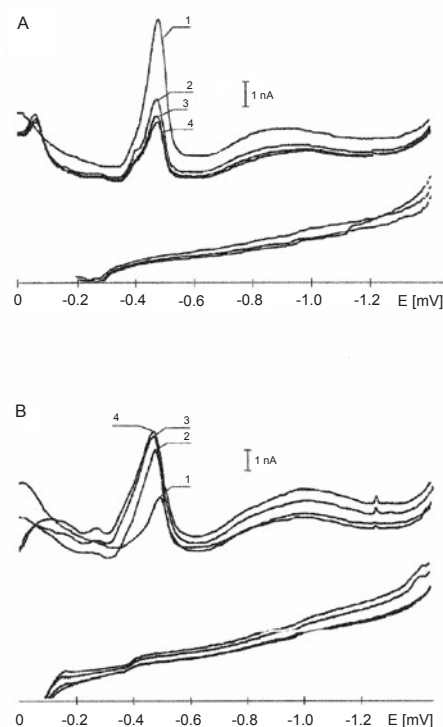
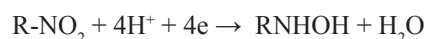


Fig.3. Cyclic voltammogram without accumulation (A:1-4, B1) and with accumulation: 5(B2), 25(B3) and 30(B4) s. Concentration of fenitrothion: 2×10^{-6} mol l⁻¹, scan rate: 100mV s⁻¹.

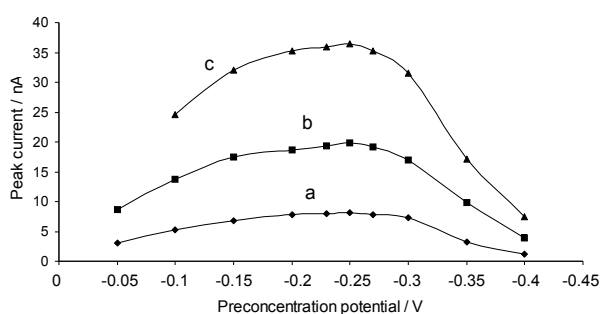


Fig.4. Effect of preconcentration potential on peak current of fenitrothion . Concentration of fenitrothion: 1(a), 2(b) and 5(c) $\times 10^{-7}$ mol l $^{-1}$; accumulation time: 30 s.

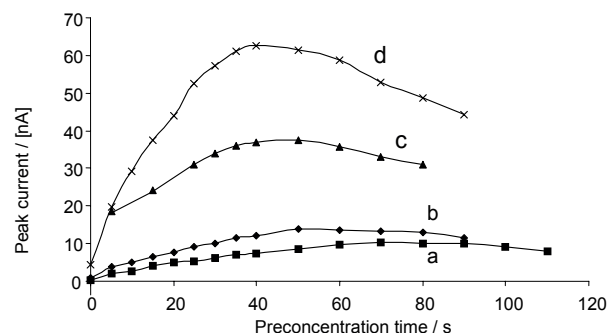
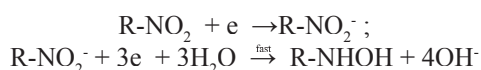


Fig.5. Effect of accumulation time on peak current of fenitrothion. Concentration of fenitrothion: 0.5(a), 1(b) 2(c) and 5(d) $\times 10^{-7}$ mol l $^{-1}$; accumulation potential: -0.20 V.

In alkaline solution the adsorption of the sulfur probably due to the electrochemical mechanism [16]:



The cyclic voltammogram behavior of fenitrothion was studied at concentration level of 2×10^{-6} mol l $^{-1}$ (at pH

7.2). Cyclic voltammograms showed one clearly defined reduction peak at -0.48 V (Fig.3A). No peaks were observed on the reverse scan, indicating the irreversibility of electrode processes. The height of the peak decreased with repetitive scans, its potential not being shifted.

When accumulation at -0.1 V was carried out, the reduction peaks were higher than those obtained without accumulation as a result of the adsorption of the initial com-

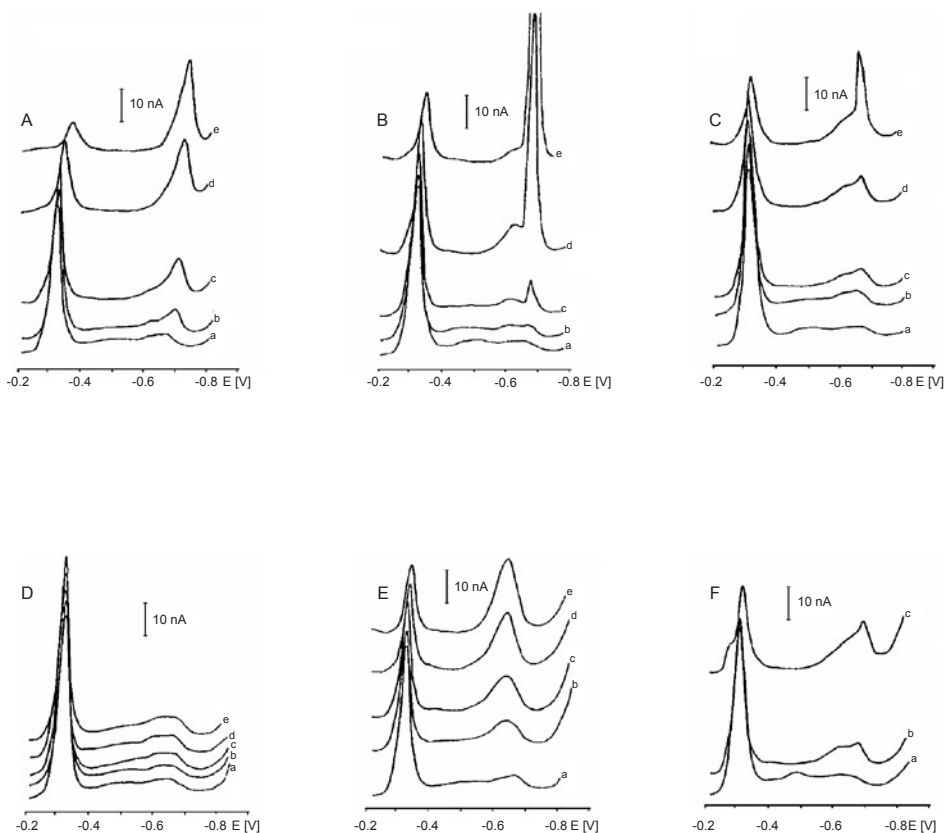


Fig.6. The influence of chlorfenvinphos CFV (A), chlorpyrifos CP (B), chlorpyrifos methyl CPM (C), dimethoate D (D), malathion M (E) and a mixture of all these compounds (F) on differential pulse stripping voltammograms of fenitrothion in 0.04 mol l $^{-1}$ Britton-Robinson buffer at pH 7.0. Accumulation time: 30 s, accumulation potential: -0,23 V. Concentration of fenitrothion: 2×10^{-7} mol l $^{-1}$; concentration of CFV, CP, CPM, D, M: 0(a), 4(b), 8(c), 20(d) and 40(e) $\times 10^{-7}$ mol l $^{-1}$; concentration of each compound of the mixture: 0(a), 2(b) and 4(c) $\times 10^{-7}$ mol l $^{-1}$.

pounds on to the mercury drop (Fig.3B). The peak potential did not change significantly, indicating that fenitrothion was not strongly adsorbed on the electrode surface.

The effects of potential scan rate (v) on the peak current and peak potential in the case of linear sweep voltammetry were evaluated. The slope of the $\log i_p$ versus $\log v$ plots, within the range 2-200 mV s^{-1} , was 0.48; this value is theoretically expected for systems controlled by diffusion. A slope of 1.0 is expected for reactions of surface active species and a slope of 0.5 for a system controlled by diffusion [17-19]. With the sulfur-containing substances, it has been reported that the sulfur itself interacts with mercury [20].

The sensitivity of adsorptive stripping voltammetry depends on the preconcentration time and preconcentration potential. A series of preconcentration potentials between -0.05 and -0.40 V were studied. Fig. 4 shows that the best preconcentration potentials are between -0.20 and -0.26 V. At potentials lower than -0.30 V the peak current decreases considerably.

Fig. 5 shows that increasing current response is observed from 0 to 40, 50 or 70 seconds for 5, 2, and 1×10^{-7} mol l^{-1} , respectively.

The calibration graph for an accumulation time of 60 seconds was linear in the range from 1×10^{-8} to 1×10^{-6} mol l^{-1} and obeyed the equation $y = 0.129x + 0.163$, where y and x are the peak current (nA) and fenitrothion concentration (nmol l^{-1}), respectively. In spiked water containing 138.6 ng l^{-1} of fenitrothion the relative standard deviation was 4.3% (for 5 determination). The detection limit, estimated from 3 times the standard deviation, was 36 ng l^{-1} . The adsorptive stripping differential pulse voltammetry can be successfully used for fenitrothion determinations in water with good precision of results.

A possible interference with fenitrothion determination from the following organophosphorous insecticides: malathion, chlorfenvinphos, chlorpyrifos methyl and dimethoate was examined (Fig. 6). Dimethoate shows no influence on peak current of fenitrothion even at 10-fold excess. Other above-mentioned insecticides caused lowering of the fenitrothion peak. This effect was observed in the case of malathion at equal concentrations, in the case of chlorfenvinphos being in two-fold excess and in the case of chlorpyrifos and chlorpyrifos methyl being in three-fold excess.

Acknowledgements

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