

Electrochemical Study of the Pesticide Methidathion at a Mercury Electrode Under Cathodic Stripping Mode

Valentin Mirčeski,^{a,*} Dariusz Guziejewski,^b Slawomira Skrzypek,^b and Witold Ciesielski^b

^a*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University in Skopje, P. O. Box 162, 1000 Skopje, Republic of Macedonia*

^b*Department of Instrumental Analysis, University of Łódź, Pomorska 163, 90-236 Łódź, Poland*

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Abstract. Methidathion, a non-systemic organophosphorous insecticide and acaricide is studied at the hanging mercury drop electrode under cathodic stripping mode by means of cyclic and square-wave voltammetry (SWV). Its electrode reaction is analyzed in the light of recent theory of cathodic stripping processes of insoluble salts of SWV. Its complex electrode mechanism is described by an electrode reaction of a second order, complicated by adsorption of methidathion molecules on the electrode surface involving lateral interactions between each other. Moreover, under specific experimental conditions the electrode mechanism can be additionally complicated by multilayer formation on the electrode surface, as well as by a chemical transformation following the cathodic stripping process of the methidathion-mercury salt. Following the mechanistic study of the electrode reaction, a method for quantitative determination of methidathion is proposed applying SWV.

Keywords: Methidathion, cathodic stripping, square-wave voltammetry

INTRODUCTION

Methidathion (S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazolyl-3-methyl O,O-dimethylphosphorodithioate) (meth), is a non-systemic organophosphorous insecticide and acaricide with a stomach and contact action (Figure 1). The compound is used to control a variety of insects and mites in many crops such as fruits, vegetables, tobacco, alfalfa, and sunflowers, as well as on rose cultures in greenhouses. It is especially useful against scale insects. Its action is based on inhibition of certain enzymes in the target pests.¹

There are several different methods for determination of methidathion. Determination at a trace level has mainly been performed by chromatographic methods employing selective nitrogen phosphorus detector or electron capture detectors.² For determination of higher methidathion concentrations, as well as for identification of its residues, chromatography coupled with mass spectrometry³⁻⁴ has been employed. Another set of relevant analytical data have been provided by thin layer chromatography⁵ coupled with electron impact ionization and mass spectrometry. From other analytical methods for determination of methidathion worth of noticing is the colorimetric method⁶ as a means for fast qualitative detection.

Up to date only one electrochemical study was presented referring to determination of methidathion at a carbon paste electrode modified with cobalt phthalocyanine and cholinesterase enzyme membrane.⁷ It is worth noting that many other pesticide compounds⁸ such as dithiocarbamate,⁹ buprofezin,¹⁰ imidacloprid,¹¹ molinate¹² and 2-thiocyanomethylthiobenzothiazole¹³ have been intensively studied on a hanging mercury drop electrode (HMDE) by means of adsorptive stripping voltammetry. Another group of pesticides, as metamitron,¹⁴ bendiocarb,¹⁵ nabam,¹⁶ and fenitrothion¹⁷ were studied on a glassy carbon electrode with, or without modification of the electrode surface. Carbaryl is a single example for the use of a boron doped diamond electrode for pesticide determination in natural waters.¹⁸

In the current communication we present a study of methidathion on a HMDE under cathodic stripping

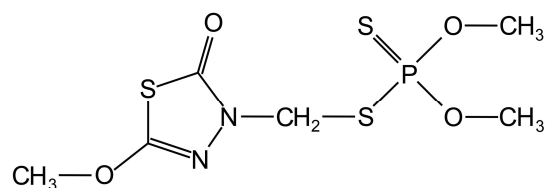


Figure 1. Molecular structure of methidathion.

* Author to whom correspondence should be addressed. (E-mail: valentin@iunona.pmf.ukim.edu.mk)

mode. The electrode mechanism is analyzed in the light of recent theories for cathodic stripping processes of insoluble salts under conditions of square-wave voltammetry (SWV).¹⁹ In the last decade significant efforts have been devoted to develop the theory of SWV for a variety of electrode mechanisms involving formation of insoluble compounds with the electrode material,^{20–24} due to the importance of these processes in the drug and pesticide electroanalysis.^{25,26} In the current communication mechanistic aspects of the electrode reaction of methidathion at the HMDE are addressed. Based on the knowledge of the electrode reaction mechanism a quantitative method for determination of methidathion is proposed by means of cathodic stripping square-wave voltammetry.

EXPERIMENTAL

All chemicals used were of analytical reagent grade. Methidathion was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany), and other chemicals were from Sigma Aldrich. A fresh stock solution of 1.00×10^{-3} mol L⁻¹ was prepared daily by dissolving 30.23 mg of the compound in a mixture of 50 mL water and 50 mL ethanol. 0.2 mol L⁻¹ MOPS buffers (pH = 6.5–7.9) or 0.04 mol L⁻¹ Britton–Robinson buffers (pH = 3.8–8.0) were used as supporting electrolytes. The general procedure to obtain cathodic stripping voltammograms was as follows: 10 mL of the supporting electrolyte was placed in the voltammetric cell and the solution was purged with argon for 10 min. When an initial blank was recorded, an appropriate volume of methidathion stock solution was added by means of a micropipette. The solution was de-oxygenated for 30 s, a new Hg drop was formed, and the voltammogram was recorded in a cathodic potential direction. Prior to the application of the cathodic sweep, an accumulation step was applied for a certain period of time at a positive potential. The other parameters of the voltammetric procedure are indicated in the captions of the figures.

All voltammetric experiments were performed on a microAutolab/GPES (General Purpose Electrochemical System, Version 4.8, Eco Chemie) computer-controlled electrochemical system. A controlled growth mercury drop electrode (Entech s.c, Cracow, Poland) was used. All potentials were referred vs. Ag/AgCl (3 mol L⁻¹ KCl) reference electrode. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

At both mercury and glassy carbon electrodes methidathion is an electrochemically non-reducible compound. At a HMDE a voltammetric response commences

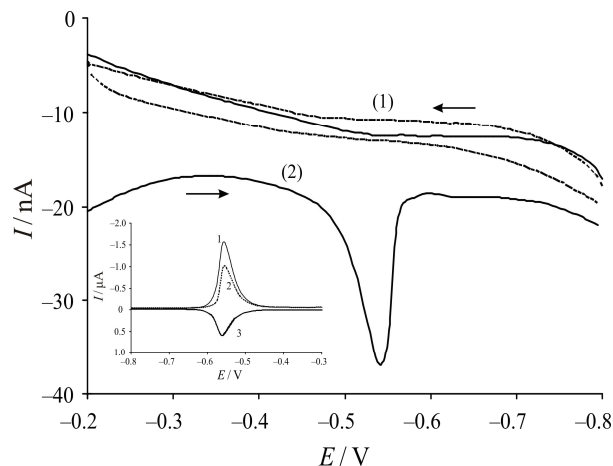


Figure 2. Typical cyclic voltammograms of 5×10^{-6} M methidathion recorded in 0.01 M MOPS buffer at pH = 7.9 and scan rate $\nu = 50$ mV s⁻¹. The potential interval was from -0.8 to -0.2 V (1, dotted line) and from -0.800 to 0.300 V (2, full line). To avoid the large current due to oxidation of mercury at positive potentials, (2) shows only a part of the cyclic voltammogram. The inset shows a typical SW voltammetric response recorded after accumulation for $t_{ac} = 30$ s at accumulation potential $E_{ac} = 0.2$ V, frequency $f = 25$ Hz, amplitude $E_{sw} = 25$ mV, and potential step $\Delta E = 5$ mV. The numbers (1), (2) and (3) of the inset refer to the net, forward, and backward component of the SW voltammetric response, respectively.

emerging only if the reductive potential sweep is preceded by a certain resting period at a potential equal, or more positive than 0.200 V. Under cyclic voltammetry conducted over the potential window from -0.800 to -0.200 V, no voltammetric response has been observed due to a faradaic electrode process (curve 1 in Figure 2). However, if the potential window is extended up to the 0.200 V, a well developed cathodic peak appeared in the reverse cathodic potential sweep (curve 2 in Figure 2). Under conditions of SWV, following the accumulation at a potential of 0.200 V, a well developed response was measured under cathodic stripping mode, with a net SW peak potential at about $E_p = -0.53$ V (see the inset of Figure 2). Replacing the mercury electrode by a glassy carbon, while keeping other conditions unaltered, no voltammetric peak was observed due to a faradaic electrode process over the whole potential window (Figure 3). Hence, from this initial set of results it can be inferred that the voltammetric activity of methidathion at a mercury electrode is a consequence of a partial oxidation of the mercury electrode followed by a formation of a film of methidathion molecules covalently bounded to the electrode surface, or formation of a sparingly soluble compound with the mercury ions, which is deposited on the electrode surface. The overall mechanism can be rationalized by considering the theory of cathodic stripping processes of insoluble salts,^{20–24} or by

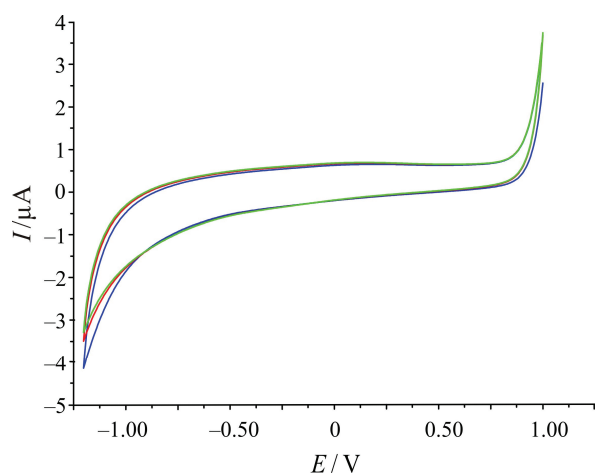


Figure 3. Typical cyclic voltammetric response recorded at a glassy carbon electrode over the potential interval from 1.00 to -1.20 V. The experimental conditions were: $\nu = 50$ mV/s, $c(\text{meth}) = 5 \times 10^{-5}$ M, MOPS buffer at pH = 7.9.

the theory of electrosorption processes and formation of a self-assembled layer on the mercury electrode.²⁷ The complexing ability of methidathion has been recently studied²⁸ providing evidences for complexation with Ca^{2+} , Mg^{2+} , Ni^{2+} and Cu^{2+} ions. These results are in accord with our electrochemical data, which indicate either chemical interactions of methidathion with the mercury electrode surface or formation of an adsorbed complex with mercury ions formed under anodic polarization in the vicinity of the electrode.

The cathodic stripping voltammetric response of methidathion depends on several experimental factors such as the composition and pH of the medium, time and potential of the accumulation preceding the cathodic stripping scan, concentration of methidathion, as well as the parameters of the potential modulation. The cathodic stripping response of methidathion can be measured over the pH interval from 6.6 to 8. An increase of pH over the latter interval caused the cathodic SW stripping peak to increase non-linearly with pH. A comparative analysis carried out in Britton-Robinson and MOPS buffers revealed that the latter provides better results, considering the peak current-to-half peak width ratio ($\Delta I_p / \Delta E_{p/2}$) as a criterion for the analytical utility. Hence, from an analytical point of view the best medium is a MOPS buffer at pH = 7.9. In addition to the peak current, the position of the cathodic stripping peak depends markedly on pH. The net SW peak potential depends linearly on pH with a slope of -59 mV/pH (data not shown). It means that the electrochemical formation of a mercury-methidathion compound is preceded by a deprotonation of the methidathion, where the number of protons equals the number of electrons exchanged in the cathodic stripping electrode reaction.²⁷ It is worth mentioning that the net SW peak depends

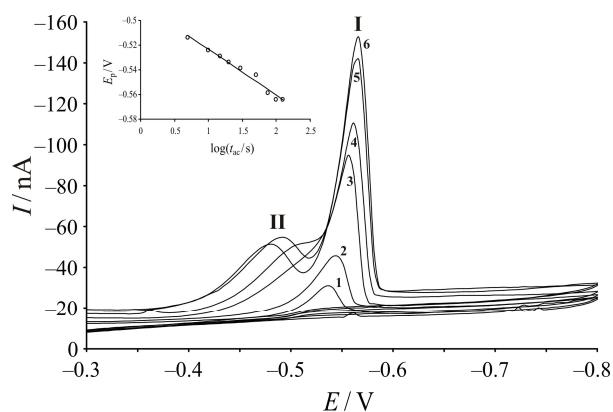


Figure 4. Evolution of the net SW cathodic stripping peak with the accumulation time. The accumulation time was $t_{ac} = 20$ (1), 40 (2), 80 (3), 100 (4), 120 (5), 150 s (6). The inset shows the dependence of the peak potential E_p for the peak (I) on the logarithm of the accumulation time. All other conditions were the same as for Figure 2.

also on the concentration of the methidathion. Over the concentration interval from 2×10^{-7} to 9×10^{-6} mol L⁻¹, the peak potential is a linear function of $\log(c(\text{meth}))$ with a slope of -15 mV ($r = 0.987$), which is typical for quasireversible second order cathodic stripping processes.²³

The morphology of the SW cathodic stripping peak depends markedly on the accumulation time. Figure 4 depicts the evolution of the net SW peaks by increasing the accumulation time from 10 to 150 s, for accumulation carried out at a potential of 0.200 V and 5×10^{-6} mol L⁻¹ concentration of methidathion. Interestingly, an increase of the accumulation time causes the net SW peak to enlarge and to shift toward more negative potentials (see peak I in Figure 4). As shown in the inset of Figure 4, the peak potential, referring to peak I, is a linear function on the logarithm of the accumulation time with a slope of -38 mV. Such intriguing behavior of the position of the net SW peak is typical for complex cathodic stripping processes complicated by lateral interactions of deposited species on the electrode surface. The phenomenon was initially observed in the cathodic stripping voltammetry of uracil, being thoroughly theoretically elaborated in our recent study.²⁶ The negative slope of the line E_p vs. $\log(t_{ac})$ reveals significant attractive forces between deposited species.²⁶

Moreover, at $t_{ac} > 60$ s a shoulder of the peak I starts emerging, which develops into the new peak II at $t_{ac} \geq 120$ s (Figure 4). The critical time at which the peak II arises depends on the concentration of the analyte. Increasing the concentration of the analyte causes the critical accumulation time to decrease, indicating clearly that the overall phenomenon depends on the surface concentration of the deposited material on the electrode. A similar phenomenon has been observed with other

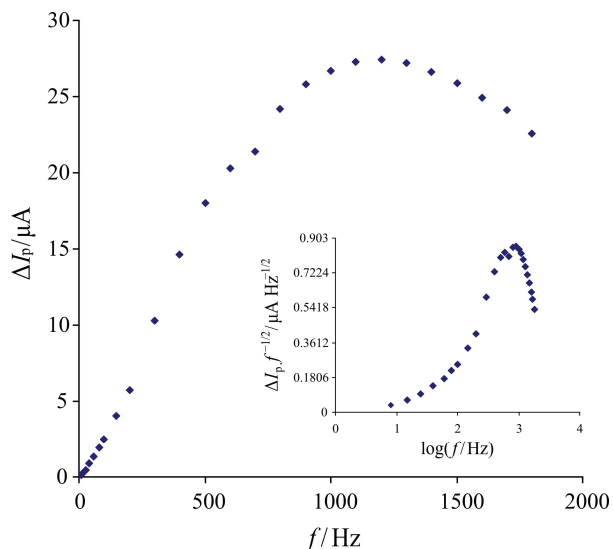


Figure 5. The effect of the frequency f on the net SW cathodic stripping peak currents ΔI_p . The inset shows the quasireversible maximum of methidathion. All other conditions were the same as for Figure 2.

sulfur containing cathodic stripping active compounds,^{29,30} which can be rationalized by considering a multilayer film formation on the electrode surface. The cathodic stripping of the initial layer directly adhered to the electrode surface requires higher energy (peak I in Figure 4) compared to other subsequent layers (peak II). From an analytical point of view formation of a multilayer film is unfavorable phenomenon and it should be avoided.

The analysis of the system by varying the parameters of the potential modulation, in particular the SW frequency (f), provides further insight into the mechanistic aspects of the electrode reaction. Generally speaking, frequency exhibits a profound effect on both peak currents and potentials of the cathodic stripping response. As typical for electrode processes complicated by surface phenomena,²⁴ the net peak currents depend non-linearly on the frequency (Figure 5). Plotting the frequency normalized net peak currents ($\Delta I_p / \sqrt{f}$) vs. $\log(f)$ one obtains a parabola-like curve (the inset of Figure 5), representing the feature known as the "quasireversible maximum" of the cathodic stripping electrode processes.²⁴ The physical meaning of the quasireversible maximum is seen in the synchronization of the electrode reaction rate with the frequency of the potential modulation, i.e., the duration of SW potential pulses. The critical frequency, f_{\max} , associated with the position of the maximum is directly proportional to the standard rate constant of the electrode reaction. As the position of the maximum is located at very high frequency of about 1000 Hz, the electrode reaction is very fast, characterized by a standard rate constant ranging in the interval $k_s > 0.2 \text{ cm s}^{-1}$.²² Besides, the SW frequency

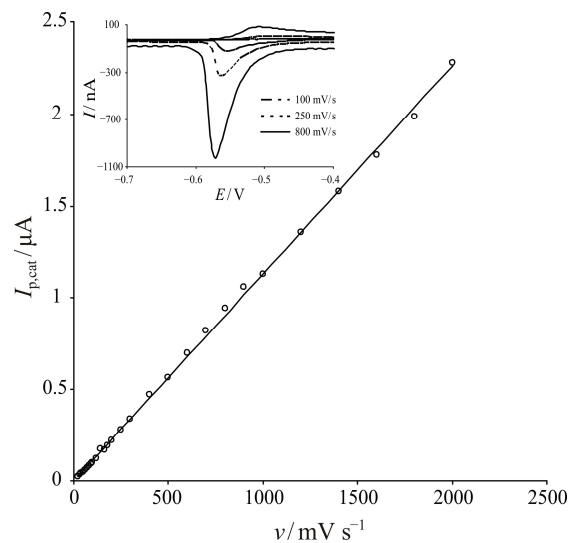


Figure 6. The dependence of the cathodic peak currents of cyclic voltammograms on the sweep rate recorded over the potential interval from 0.200 to -0.800 V . All other conditions were the same as for Figure 2. The inset shows a part of the cyclic voltammograms recorded at different sweep rates indicated on the plot.

affects significantly the position of the net peak. The dependence E_p vs. $\log(f)$ is associated with a linear function with a slope of -39 mV ($r=0.989$), which agrees well with the theoretical predictions for quasireversible cathodic stripping processes.^{20–24}

The complexity of the electrode mechanism has been further revealed by analyzing the morphology of the voltammetric response by varying sweep rates of the cyclic voltammetric experiment. The results of the

Table 1. Basic statistic data of the linear regression line, together with the limit of detection (LOD) and the limit of quantification (LOQ) of the method. The experimental conditions were: accumulation time $t_{\text{ac}}=30 \text{ s}$, accumulation potential $E_{\text{ac}}=0.2 \text{ V}$, frequency $f=50 \text{ Hz}$, amplitude $E_{\text{sw}}=25 \text{ mV}$, potential step $\Delta E=5 \text{ mV}$ and scan range from 0.2 to -1.2 V

	SWV
Linear concentration range / $\mu\text{mol L}^{-1}$	0.2 – 3.85
Slope of calibration graph / ($\text{mA} / \text{mol L}^{-1}$)	41.1
RSD of slope	0.055
Intercept / nA	4.99
Correlation coefficient	0.998
RSD of intercept	0.027
Number of measurements	6
LOD / nmol L^{-1}	98.5
LOQ / nmol L^{-1}	128
Repeatability (RSD %)	4.4
Reproducibility (RSD %)	4.9

Table 2. The precision and recovery data for the determination of methidathion with cathodic stripping SWV. Experimental conditions were the same as for Table 1

Added $\mu\text{mol L}^{-1}$	Found $\mu\text{mol L}^{-1}$	Precision %	Recovery %	Number of experiments	Bias %
0.40	0.37 ± 0.04	6.8	92.5	6	7.5
1.48	1.41 ± 0.07	5.7	95.3	6	4.7
3.85	3.66 ± 0.22	5.8	95.1	6	4.9

sweep rate analysis are summarized in Figure 6. Over the sweep rate interval from 20 to 2500 mV/s, the cathodic stripping peak is a linear function on the sweep rate ($r=0.999$), which is typical for all non-diffusional electrode processes where the reactant is immobilized on the electrode surface.³¹ Analysis of plot $\log I - \log v$ gives the equation: $I/\mu\text{A} = 1.0361 v/\text{mV s}^{-1} - 3.049$, $r=0.999$ and confirms that this process is adsorption controlled.³² For better clarity, we note that the experiments have been performed by cycling the potential from 0.200 to -0.800 mV. If the scan rate was $v < 250$ mV/s, the cyclic voltammograms feature only a single cathodic stripping peak without an anodic peak in the reverse scan. If $v \geq 250$ mV/s the anodic peak commences arising with a peak height proportional to the sweep rate. Such intriguing voltammetric behavior is typical for an EC_i reaction scheme, where the electrode reaction (E) is followed by an irreversible chemical reaction step (C_i). To the best of our knowledge this is the first experimental case where the cathodic stripping mechanism of an insoluble salt is additionally complicated by a follow-up chemical step. For such complex processes particular theoretical model is yet undeveloped, being a challenge for a new theoretical consideration in future. It is worth noting that under conditions of SWV, which is a very fast voltammetric method, the effect of the following chemical reaction is insignificant even at the lowest frequency of 8 Hz available by the instrumentation.

Finally the effect of the concentration on the net SW peak has been studied in order to establish a basis for development of a quantitative method for determination of methidathion by means of cathodic stripping SWV. Electrochemical techniques, such as linear sweep voltammetry, differential pulse voltammetry or square wave voltammetry have been widely applied for the determination of compounds of biological interest.^{33–36} Under optimal instrumental parameters such as SW amplitude (25 mV), frequency (50 Hz), accumulation time (30 s) and accumulation potential (0.2 V) the linear dependence of net SW peak current on methidathion concentration in the range from 2×10^{-7} – 3.85×10^{-6} mol L⁻¹ was observed. The analytical characterization of the method is summarized in Table 1. The detection limit (LOD) and quantification limit (LOQ) of the procedure were calculated from the calibration curves as $k\text{SD}/b$,

where $k=3$ for LOD and 10 for LOQ, SD is the standard deviation of the intercept, and b is the slope of calibration line.³⁷ Repeating six experiments on 2×10^{-6} mol L⁻¹ methidathion tested the repeatability (one day) and reproducibility (over a week) of peak currents. The results were shown also in Table 1. The precision, recovery and bias of the method were investigated by determination of methidathion at three different concentrations within the linear range, the results being presented in Table 2. To the best of our knowledge, this is the first cathodic stripping voltammetric method proposed for determination of methidathion. In addition the method is much more sensitive than the procedure using modified carbon paste electrode in an amperometric biosensor.⁷

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SAŽETAK

Elektrokemijsko istraživanje pesticida metidationa akumulacijom i redukcijom na živinoj elektrodi

Valentin Mirčeski,^a Dariusz Guziejewski,^b Sławomira Skrzypek^b i Witold Ciesielski^b

^a*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University in Skopje, P. O. Box 162, 1000 Skopje, Republic of Macedonia*

^b*Department of Instrumental Analysis, University of Łódź, Pomorska 163, 90-236 Łódź, Poland*

Cikličkom i pravokutnovalnom voltametrijom na stacionarnoj, sferičnoj živinoj elektrodi istražen je mehanizam elektrodredukcije metidationa, nesistemskog organofosfornog insekticida i akaricida. Spoj je akumuliran na površini elektrode kao monosloj netopive živine soli, a zatim je talog reduciran voltametrijskom pobudom. Pokazano je da je elektrodana reakcija drugog reda i da je komplicirana lateralnim interakcijama u monosloju. Pod određenim uvjetima uočeno je formiranje višeslojnog taloga i kemijska transformacija produkta elektrodne reakcije.