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A study of the electrochemical behaviour of methomyl on a gold electrode in a neutral electrolyte

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Abstract: A gold electrode was used for the qualitative and quantitative electrochemical determination of analytical methomyl in a neutral electrolyte (0.050 M NaHCO₃) using cyclic linear sweep voltammetry. In the potential range from –800 mV vs. SCE to 1000 mV vs. SCE the analytical methomyl was quantitatively determined in the concentration range 4.0–16 mg L⁻¹. In the potential range from –1300 mV vs. SCE to 1300 mV vs. SCE, methomyl was qualitatively determined by two anodic and four cathodic reactions. Cycling the potential in this range for 150 min caused the degradation of the molecule, which was confirmed by HPLC analysis. On the other hand, technical methomyl exhibited an inhibition of the gold electrode surface due to the impurities.

Keywords: insecticide; methomyl; gold electrode; cyclic voltammetry.

INTRODUCTION

Methomyl (Fig. 1) is a broad-spectrum thiocarbamate insecticide, which was introduced in 1966.¹ It is also used as an acaricide to control ticks and spiders, for foliar treatment of vegetable, fruit and field crops, cotton, commercial ornamentals, and in and around poultry houses and dairies. Furthermore, it is used as a fly bait.² Methomyl is effective in two ways: a) as a “contact insecticide” because it kills the target insects upon direct contact and b) as a “systemic insecticide” because of its capability to cause overall “systemic” poisoning of the target insects, after it is absorbed and transported throughout pests that feed on the treated plants. It is capable of being absorbed by plants without being “phyto-toxic” or harmful to the plant. It is a very toxic and hazardous compound and an

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environmental pollutant of concern because of its high solubility in water (57.9 g/L at 25 °C).³

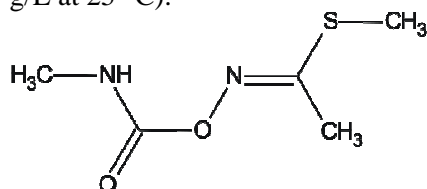


Fig. 1. Structure of methomyl; IUPAC name: *S*-methyl-*N*-(methylcarbamoyloxy) thioacetimidate.

Different thiocarbamate herbicides were the subject of electrochemical studies using different electrodes.^{4–9} Methomyl and aldicarb were detected by fast scan differential voltammetry with a hanging Hg drop electrode.⁴ Later, the electrochemical behaviour of methomyl was studied using d.c. and a.c. polarography, differential pulse polarography and cyclic voltammetry in ethanol–water mixtures. It was found that methomyl undergoes irreversible four-electron reductions.⁵ Mogyoródy^{6–8} published the results of studies of the electrochemical degradation of several thiocarbamates in NaCl solution using a Pt electrode. Pulsed amperometric detection at a gold electrode was used for the separation of eight pesticides in reversed-phase liquid chromatography, including methomyl.⁹ Current–potential curves were obtained by cyclic voltammetry at a gold, rotating-disc electrode in 50 % (v/v) acetonitrile in acetate buffer.

In studies of the degradation of organic compounds¹⁰ and the electrochemical behaviour of physiologically active compounds,^{11–13} a study the electrochemical behaviour of methomyl was included. Analytical and technical methomyl were used in order to develop an electrochemical method for the qualitative and quantitative determination of methomyl. Methomyl was examined at a gold electrode in a neutral electrolyte using cyclic linear sweep voltammetry. HPLC was used for analysing the bulk electrolyte during the electrochemical reactions.

EXPERIMENTAL

Analytical methomyl (99.8 %, analytical standard) and technical methomyl (98 %) were obtained from DuPont. Before each experiment, a fresh solution of methomyl in 0.050 M NaHCO₃ (methomyl concentration = 16 mg L⁻¹) was prepared. The solution was added directly into the cell and then purged with nitrogen during each experiment.

The NaHCO₃ used as the supporting electrolyte was of analytical grade (Merck). The solutions were prepared with 18 MΩ water. Standard equipment and a three electrode electrochemical cell were used for the cyclic voltammetry measurements, as previously described in detail.^{12–13} Polycrystalline gold (surface area 0.50 cm²), which served as the working electrode, was polished with diamond paste and cleaned with a mixture of 18 MΩ water and sulphuric acid. A platinum wire was employed as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials are given vs. SCE. The electrode surface was controlled by cyclic voltammetry before each experiment. Prior to the control of the electrode surface and before the addition of methomyl, the electrolyte was purged with nitrogen. All the experiments were performed at room temperature.

The characteristics of the HPLC instrument were as follows: HPLC Instrument GBC, pump LC 1120, UV-Vis detector LC 1205, operating at 234 nm, manual injector RHEODYNE 7725i, column ZORBAX Eclipse XDB-C8 (4.6 mm×150 mm, 5 μ m), mobile phase acetonitrile–water (25:75, flow rate 1.0 cm³ min⁻¹).

RESULTS AND DISCUSSION

The reactivity of methomyl (analytical and technical) was investigated on a gold electrode in 0.050 M NaHCO₃ by cyclic voltammetry. On a gold electrode, in the potential range from -800 mV vs. SCE to 1000 mV vs. SCE, the analytical methomyl exhibited one anodic and two cathodic reactions and the observed anodic reaction was later used for its quantitative determination. In the potential range from -1300 mV vs. SCE to 1300 mV vs. SCE, methomyl exhibited two anodic and four cathodic reactions (Fig. 2). The potential was cycled in this range for 150 min in order to follow any possible changes of these anodic and cathodic reactions with time. It is obvious from Fig. 2 that the anodic peak at 1200 mV vs. SCE increased with time from 0.46 mA cm⁻² (first cycle) to 0.80 mA cm⁻² at the end of the cycling. The anodic peak, which appeared at the beginning of oxide formation at the gold electrode, at 600 mV vs. SCE was slightly higher and shifted 30 mV to more negative potential values at the end of the cycling. The four cathodic peaks remained unchanged during the cycling.

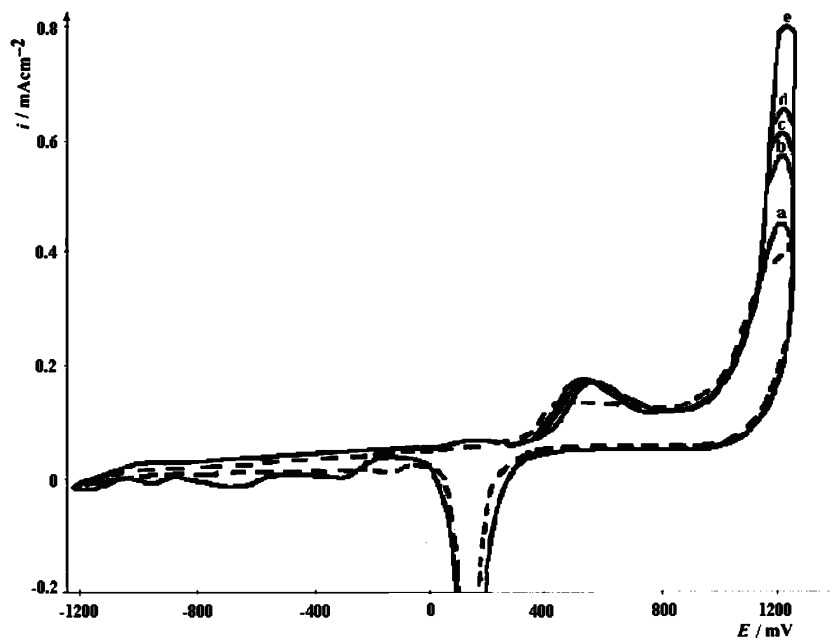


Fig. 2. Cyclic voltammogram of an Au electrode in 0.050 M NaHCO₃ (dashed line) and in the presence of the methomyl solution (concentration 16 mg L⁻¹) in 0.050 M NaHCO₃ (full line; a, 0; b, 30; c, 60; d, 90; e, 150 min of continuous cycling); sweep rate: 50 mV s⁻¹.

The observed reactions presented in Fig. 2 indicate the degradation of the methomyl molecule in 0.050 M NaHCO₃. In order to check this assumption, HPLC analysis was performed before the electrochemical experiment and after 30, 60, 90 and 150 min of potential cycling under the conditions presented in Fig. 2. The results of the HPLC analysis are presented in Figs. 3 and 4. Fig. 3 shows the change in the methomyl concentration given as normalized concentrations (c/c_0 , where c is the methomyl concentration at time t and c_0 is the initial methomyl concentration) vs. time, while Fig. 4 represents the HPLC chromatogram. As can be seen, the starting molecule, which represents the analytical product, contained only small amounts of impurities. The HPLC analysis showed a small decrease in the methomyl concentration after the electrochemical reactions (less than 6 %).

As mentioned previously, pulsed amperometric detection at a gold electrode was used for the separation of eight pesticides, including methomyl, in reversed-phase liquid chromatography, and the anodic reaction at the beginning of oxide

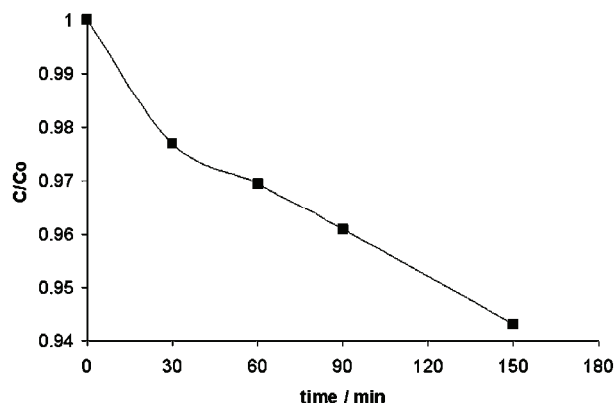


Fig. 3. Change in the methomyl concentration during potential cycling.

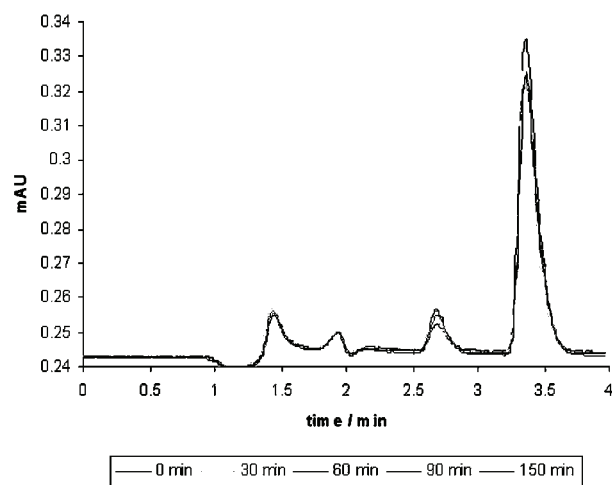


Fig. 4. HPLC chromatogram of the methomyl solution during potential cycling.

formation was used for the quantitative determination.⁹ The limit of detection for methomyl was found to be below $80 \mu\text{g cm}^{-3}$ (80 mg L^{-1}).

On the gold electrode, in the potential range from -800 to 1000 mV vs. SCE , the anodic reaction which commences at the beginning of oxide formation was used for the quantitative determination of the analytical methomyl. This range of the potential was selected in order to avoid apparent methomyl degradation at 1200 mV and two cathodic reactions in the potential range from -800 to -1300 mV .

The voltammogram presented in Fig. 5 shows that each investigated methomyl concentration gives only one very clear, wide and reproducible anodic peak in the concentration range $4\text{--}16 \text{ mg L}^{-1}$, which followed a linear relationship corresponding to the equation:

$$i_{\text{pa}} / \text{mA cm}^{-2} = 183.8 \pm 2.9 \times 10^{-3} + 3.9 \pm 0.2 \times 10^{-3} c / \text{mg cm}^{-3} \quad (1)$$

$$r = 0.9953$$

This type of the equation was successfully applied for the quantitative determination of different small concentrations of macrolide antibiotics on a gold^{14,15} and on a glassy carbon electrode.^{15–17}

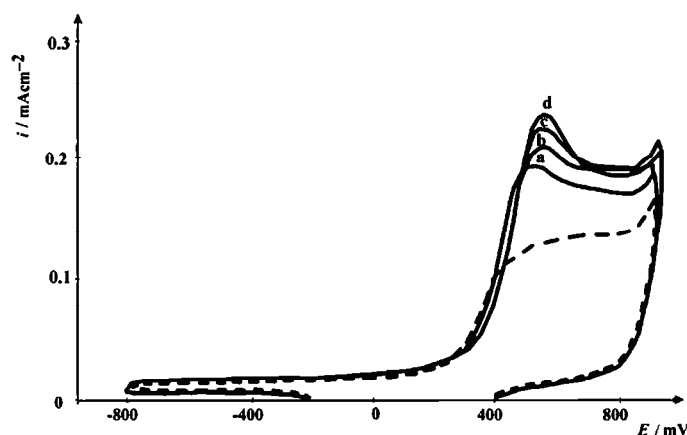


Fig. 5. Cyclic voltammogram of an Au electrode in 0.050 M NaHCO_3 (dashed line) and in the presence of the methomyl solution ($4\text{--}16 \text{ mg L}^{-1}$) in 0.050 M NaHCO_3 (full line; a, 4; b, 8; c, 12; d, 16 mg L^{-1}); sweep rate: 50 mV s^{-1} .

The obtained relationship can be used for the quantitative determination of analytical methomyl at lower concentrations in comparison to the literature value.⁹ The selected concentration range was based on the methomyl concentrations used in a previous study,¹⁰ in which the reaction of methomyl photodegradation was followed by UV spectroscopy. The standard error of the correlation was found to be 2.37×10^{-3} , while the standard deviation and the error of the measurements were 2.13×10^{-3} and $6.15 \times 10^{-4} \text{ mA cm}^{-2}$, respectively. This relationship is also given in Fig. 6.

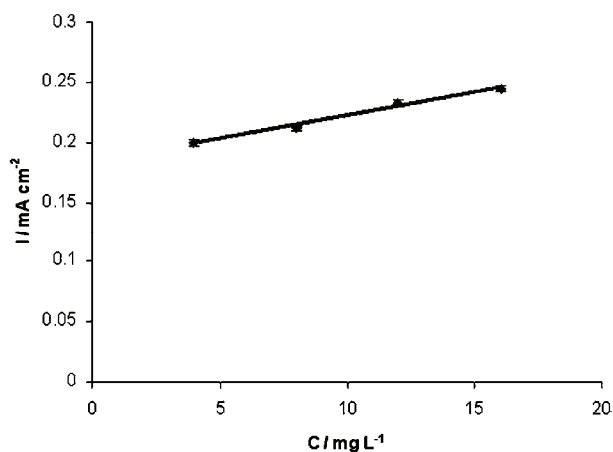


Fig. 6. Dependency of the peak current value of the oxidation peak of the analytical methomyl at 600 mV vs. SCE in 0.050 M NaHCO₃ at a scan rate of 50 mV s⁻¹, from the data presented in Fig. 5, as a function of the concentration in the range of 4–16 mg L⁻¹.

On the other hand, when technical methomyl was subjected to the same experimental conditions, an inhibition was observed due to the presence of impurities.

CONCLUSIONS

A gold electrode was successfully employed for the qualitative and quantitative electrochemical determination of analytical methomyl in a neutral electrolyte (0.050 M NaHCO₃) using cyclic linear sweep voltammetry. In the potential range from –800 to 1000 mV vs. SCE, the analytical methomyl was quantitatively determined in the concentration range 4–16 mg L⁻¹. In the potential range from –1300 to 1300 mV vs. SCE, methomyl exhibited two anodic and four cathodic reactions and its electrochemical treatment for 150 min showed the disappearance of the molecule. HPLC analysis of the bulk of electrolyte showed a decrease of the methomyl concentration because of the electrochemical reactions which had occurred. The same experiments could not be performed with the technical methomyl due to the inhibition effect of impurities present in such a product.

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ИЗВОД

ПРОУЧАВАЊЕ ЕЛЕКТРОХЕМИЈСКОГ ПОНАШАЊА МЕТОМИЛА НА ЕЛЕКТРОДИ ОД ЗЛАТА У НЕУТРАЛНОМ ЕЛЕКТРОЛИТУ

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У раду су дати резултати испитивања електрохемијског понашања активности метомила (аналитичког и техничког производа) на електроди од злата у неутралном електролиту (0,050 М NaHCO₃). HPLC је коришћена за анализу електролита у току електрохемијске ре-

акције. Максимална вредност висине струјног врха оксидације чистог метомила на 600 mV према ЗКЕ у 0,050 M NaHCO₃ на 50 mV s⁻¹ је линеарна функција његове концентрације у опсегу 4–16 mg L⁻¹ што је омогућило развијање методе за његово квантитативно одређивање. Аналитички метомил је квалитативно одређен детекцијом репродуктивне четири анодне и једне катодне реакције у опсегу потенцијала од –1300 до 1300 mV према ЗКЕ. Потенцијал је циклизиран 150 min у наведеном опсегу и анализа анодних и катодних реакција на почетку, у току и на крају циклизирања потенцијала је указала на деградацију молекула метомила. Током циклизирања потенцијала, HPLC анализа електролита је показала смањење концентрација метомила као последицу његове деградације. Технички метомил није погодан за испитивање под наведеним условима јер присутне нечистоће инхибирају површину електроде.

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