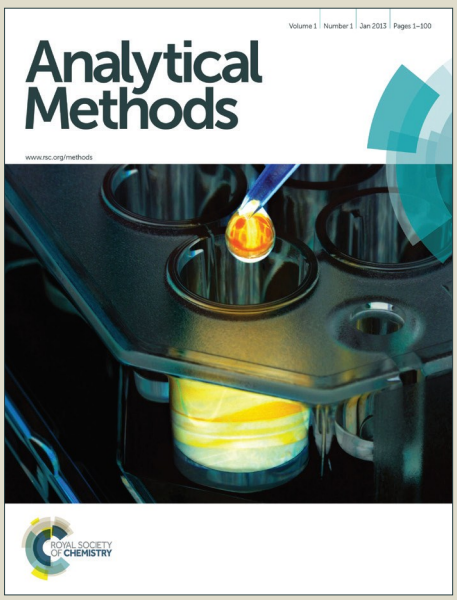
Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Analytical Methods

ARTICLE

Determination of *Methiocarb* pesticide using differential pulse voltammetry with a boron-doped diamond electrode

Received 00th March 20xx,
Accepted 00th March 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

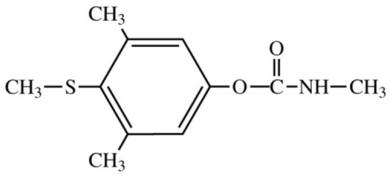
J. Chýlková[a], M. Tomášková[a], I. Švancara[b], L. Janíková[a] and R. Šelešovská[a]

In this article, a simple and rapid method is described for voltammetric determination of *Methiocarb* (*MTC*, a pesticide of the carbamate type). Direct oxidation of *MTC* at a highly positive potential of about +1.4 V vs. Ag/AgCl was found feasible thanks to the excellent performance of the working boron-doped diamond electrode in combination with the differential pulse voltammetric ramp. After optimisation of important parameters, the signal of *MTC* could be calibrated in an interval of 1-55 μg mL^{-1} *MTC*, when offering a detection limit (3 σ) of *ca*. 0.15 μg mL^{-1} *MTC*. Practical applicability of the method has been demonstrated on analyses of a commercial pesticide, either with respect to the total content of *MTC* or as its gradual and time-controlled dissolution in the model sample of natural aquatic system.

Introduction

Carbamates are one of the major classes of synthetic pesticides and due to their broad biological activities, these compounds are used on large scale around the world[1]. The most commonly used pesticide with insecticidal and molluscicidal activity is *Methiocarb* (*MTC*; 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate); see scheme. Since the 1960s, this substance has been used as pesticide for variety of invertebrate pests and also in the form of a bird repellent on fruit crops[2-4]. Outdoor use of *MTC* is likely to have adverse effects on aquatic and terrestrial species that can be divided into several groups[3-8]: from slight toxicity towards waterfowl and practical harmfulness for upland game birds, via significant impact on many species of coldwater and warmwater fish, up to high toxicity for aquatic invertebrates and honey bees.

In Czech Republic, commonly used pesticides are also organophosphates[9-11], representing, however, the compounds with the most frequent poisoning due to their substantial neurotoxic activity.



Scheme 1 *Methiocarb (MTC)*

[a] *Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic, Email: Marketa.Tomaskova@upce.cz.*
[b] *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic.*

It is quite well-known that the application of these compounds in commercial formulations is effective with respect to their rapid bio-degradability in the environment and, in general, high selectivity[2]. On the other hand, the organophosphates are rather dangerous to human health when used inappropriately or even carelessly. Similarly to the above-mentioned carbamates, the main principle of acting is an inhibition of acetylcholinesterase (ACHE) in the central nervous system[3,7]. Nevertheless, there is certain difference in the proper mechanism, when organophosphate inhibitors are bound irreversibly, whereas the carbamates are pseudo-irreversible in nature and the application of the latter is therefore more friendly from an environmental point of view. Especially this is the reason of why the latest applications of pesticides are turning in favour of carbamates, including *Methiocarb*; typical example being its use for reducing the overgrowth of zoo-plancton[9-11].

In order to monitor and control the content of *MTC*, there is an increasing demand for reliable, sufficiently sensitive, and accessible analytical methods with the respective procedures. Herein, a collection of about twenty of such approaches can be presented, comprising the employment of HPLC[12-19], gas chromatography[20-25], or the so-called QuEChERS, a special extraction methodology[26-28] that enables one to determine a wide variety of carbamates — often, in simultaneous analyses — in different types of samples.

Also electrochemical methods with typically inexpensive instrumentation are potentially applicable to the determination of various pesticides[29,30], offering a very good analytical performance in relatively simple procedures and usually without derivatisation step(s) incorporated in some chromatographic detections (see e.g. papers[17,18]). For instance, this can be demonstrated on an extensive study from the early 1980s[31], in which 13 different carbamates had been investigated with respect to their electrochemical activity and

solely a quartet of compounds — namely, in alphabetical order: *Aminocarb, Methiocarb, Pirimicarb*, and *Zectran* — were found to give rise to measurable oxidation waves. The electroactive pesticides could be detected in buffered aqueous and methanolic solutions with the glassy carbon electrode (GCE). Regarding *Methiocarb*, its oxidation signals appeared superposed upon the oxygen evolution wave, but their mutual resolution had varied from case to case, depending on the actual background current (or "signal-to-noise ratio", resp.) and the measuring mode, when e.g. determination in flowing streams was found impossible.

Ni et al.[32] reported on the determination of four carbamate pesticides; namely, *Carbaryl, Carbofuran, Isoprocarb*, and *Propoxur* in various water samples. Also in this case, the GCE was used combined with differential pulse voltammetry (DPV), when diluted perchloric acid had served as the supporting electrolyte of choice. As the voltammetric signals of the individual analytes largely overlapped and the resultant responses exhibited mostly non-linear character, various chemometric calibration models had to be applied in order to facilitate simultaneous determination of the individual analytes.

In a recent study[33], Inam and Bilgin examined voltammetric determination of *Methiocarb* with a new type of (multiwalled) carbon nanotube electrode in combination with square-wave voltammetry (SWV). After inevitable optimisation, the signal(s) of interest could be calibrated in 0.1 mol L^{-1} H_2SO_4 over the concentration range of 1.5-59.1 mg L^{-1} MTC and with a detection limit of 0.45 mg L^{-1} *MTC*. The resultant method was characterised as simple, fairly insensitive to matrix effects, when the analyte could be determined in a commercial insecticide (formulation), as well as selected samples of natural water and polluted soil.

Finally, there is a study performed with boron-doped diamond-based electrodes (BDDEs[34]) capable of achieving a highly effective detection of four selected carbamates: *Bendiocarb*, *Carbaryl, Carbofuran,* and *methyl 2-benzimidazole-carbamate*, after their chromatographic separation. It has been confirmed that the conductive diamond applied in the form of a thin film attached to the GCE substrate is a *de luxe* sensing material, when the corresponding electrodes were found to be far superior to other carbon-based configurations. The BDDEs exhibited stable and sensitive responses for all carbamate pesticides of the phenolic family despite the high oxidation potentials needed. At low(er) potentials, their performance was yet even better for almost all electroactive pesticides tested.

This article reports on the electrochemistry and voltammetric determination of *Methiocarb* at such a BDDE, belonging for more than a decade among the most popular electrode configurations in current-flow / faradic measurements[35-37]. As shown in the following sections, the choice of this electrode and the elaboration of the respective method allowed us to obtain simple and quickly-to-use tool to determine *Methiocarb* in two samples of environmental character – in a commercial product and pond water.

Experimental

Chemical and reagents

Standard solutions of the substance of interest were made in a wide concentration range from 3.22 mg L^{-1} up to 980 mg L^{-1} by dissolving the appropriate amount of *Methiocarb* (*MTC*; 99.5%, Merck) in methanol (p.a. grade; Penta, Chrudim, Czech Republic); all these solutions being stored in a dark place at 4 °C.

The following stock solutions were used for adjusting the desired pH during measurements: (i) 1 mol L^{-1} sulphuric acid (prepared from 96 % H_2SO_4; Penta, Chrudim, CZ), eventually, an adequately pipetted volume of conc. H_2SO_4 diluted 1:1; (ii) 1 mol L^{-1} chloroacetate buffer with pH 3.50 and containing monochloroacetic acid (Lachema Brno, CZ) + appropriate amount of 4 mol L^{-1} NaOH); (iii) 1 mol L^{-1} acetate buffer, pH 4.53, prepared from sodium acetate and acetic acid (both p.a. grade, Lachema); (iv) 1 mol L^{-1} citrate buffer, pH 6.62, made from crystalline citric acid (p.a. grade, Penta) and appropriate amount of 4 mol L^{-1} NaOH; (v) 1 mol L^{-1} phosphate buffer, pH 7.50, containing sodium hydrogen phosphate (Na_2HPO_4; p.a. grade, Lachema) with the addition of phosphoric acid (65% H_3PO_4; Lachema) with the addition of diluted NaOH.

If not stated otherwise, the determination of *MTC* was performed in mixed media, containing 10% (v/v) MeOH. Regarding the commercial product selected for the first testing analysis, a weighted portion of *Mesurol®* ("Schneckenkorn"; AgroBio Opava, CZ) served as one of the real samples.

Apparatus, Electrodes, and Other Instrumentation

Voltammetric analyses were performed using an electrochemical analyser (model "EP 100VA", HSC Servis Bratislava, Slovakia) in connection with the 3-electrode cell comprising the working BDDE, an Ag|AgCl|3 M KCl reference, and a Pt-plate (3×5 mm) as the counter electrode (both Monokrystaly Turnov, CZ). The boron-doped diamond electrode was represented by an electrode chip configuration described previously[38,39] and consisting of a BDD film lithographically deposited onto the Si-wafer substrate, tailored into a disc shape and so fixed in plastic body (with inner diameter, ∅ = 3 mm). Its resistivity was 0.075 Ω×cm at the boron doping level of 1000 ppm as declared by the producer (Windsor Scientific Ltd., UK).

Whenever needed, pH of solutions to be analysed was measured with an InoLab E-meter (model "pH 720"; WT Werke, Germany) equipped with the combined glass pH-electrode ("Sen Tix 41" type; the same manufacturer).

Voltammetric Procedure(s)

Determination of *Methiocarb* was performed in the differential pulse voltammetric mode (DPV) by direct measurement — i.e., without accumulation —, and when using the instrumental setting listed in Table 1. (Most of these parameters were set based on our previous experience with measurements of similar substances.)

Table 1 Instrumental parameters for DPV measurement

Parameter / Mode	Setting
Potential ramp	DPV
Current range	±4 µA
Initial potential, E_{in}	+0.4 V
Final potential, E_{fin}	+ 1.7 V
Scan rate (v)	40 mV s^{-1}
Pulse amplitude (height)	30 mV
Pulse length (increment)	60 ms

A typical analysis then proceeded as follows: Into a mixture of 200 µL conc. H_2SO_4 (1:1) + 1 mL MeOH in a voltammetric vessel, 9 ml water (or adequate volume of the respective sample) were added and left purged by bubbling with inert gas for ca. 5 min. Then, all three electrodes were shortly rinsed with distilled water and the cell assembled for measurement. After checking the set-up of all instrumental parameters (see Table 1), the model / sample solution (10 mL in total volume) was analysed by scanning the potential ramp in the anodic direction and the signal of interest at about +1.4 V vs. Ag/AgCl registered. In the case of serial analyses, the scanning was repeated as required. (Note: Meanwhile, no special regeneration or mechanical cleaning of the working BDDE was needed.) Last but not least, the concentration of MTC was quantified by means of the standard addition method with multiple aliquots.

Results and Discussion

Optimisation of conditions for *MTC* determination

From the literature data it was evident that voltammetric detection of *Methiocarb* would require an electrode with sufficiently wide potential window during the anodic scanning like that reported for (electrocatalytically acting) nanotube-based sensor[33]. Similarly to this, also the boron-doped diamond might offer comparable polarisation capabilities with generally low background currents, which was one of the reasons why the BDDE had been selected for the study presented herein. Its other benefits then came along: the chemical stability, biological biocompatibility, and mechanical resistance[36,37,40]; all representing important aspects for practical electroanalysis. Finally, for electroactive pesticides, the same working electrode has also been successfully used previously[38,39].

At first, the anodic oxidation of *Methiocarb* was studied in dependence on the pH varied. The respective measurements were carried out in six solutions; namely: (i) 0.1mol L^{-1} H_2SO_4; (ii) 0.1 mol L^{-1} chloracetate (pH 3.50), (iii) 0.1 mol L^{-1} acetate (pH 4.53), (iv) 0.1 mol L^{-1} citrate (pH 6.62), and (v) 0.1 mol L^{-1} phosphate buffer (pH 7.20) plus (vi) 0.1 mol L^{-1} NaOH, completing the set. Regarding the concentration of the pesticide, it was intentionally varied in an interval from 9.70 µg mL^{-1} to 80.92 µg mL^{-1} *MTC.*

Based on the observations made, it can be stated that the increasing pH — i.e., the lower acidity — has given rise to the enhanced sensitivity of the detection except highly alkaline media of sodium hydroxide with no evident response. Fig. 1 documents this behaviour, illustrating two sets of calibration voltammograms for the oxidation of *MTC* in 0.1 mol L^{-1} H_2SO_4 (A) and citrate buffer (B); both experiments resulting in a linear dependence between the peak height and concentration of *MTC* up to certain limit (see below).

The corresponding regression equations, along with the other ones calculated from the analyses of the remaining solutions have been evaluated with the aid of statistical program "Adstat"[41] and are given in Table 2, together with the individual correlation coefficients and detection characteristics summarising the results of this key study. By comparing the data in the table and taking the widest linearity as the criterion of primary importance, acidic media of 0.1 mol L^{-1} H_2SO_4 were selected for further measurements, allowing us to calibrate the system up to 55 µg mL^{-1}. In order to widen the linearity range as much as one could get, the next assay was focused on the effect of the increasing content of methanol, MeOH, in the sample solution; herein, in mutual mixtures with 0.1 mol L^{-1} H_2SO_4 as the electrolyte of choice (see above).

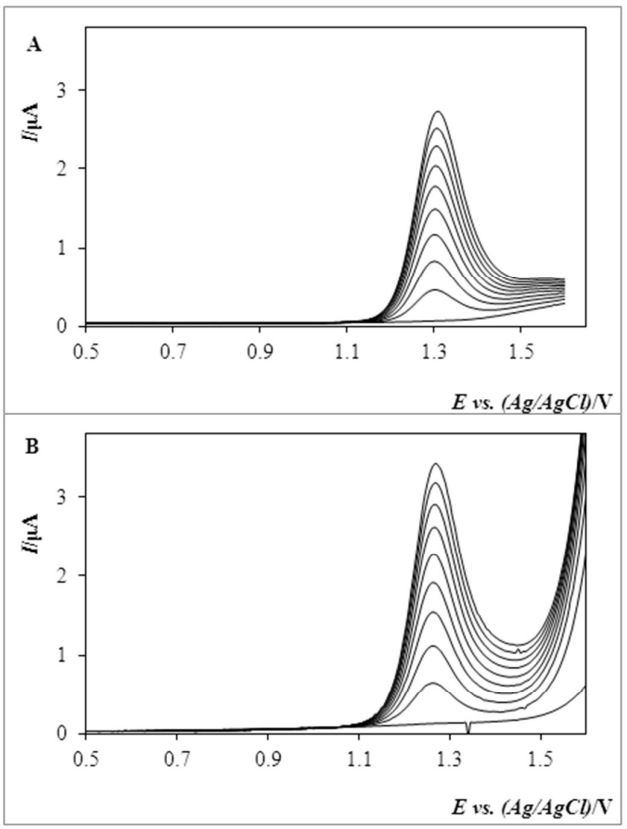


Fig. 1 DP-voltammograms of *MTC* in the supporting electrolyte of (A) 0.1 mol L^{-1} H_2SO_4 and (B) 0.1 mol L^{-1} citrate buffer with pH 6.62. Exp. conditions: DPV ramp, E_{in} +0.3 V, E_{fin} +1.6 V, scan rate: 40 mV s^{-1}, *MTC* in concentration range from 9.7 µg mL^{-1} to 80.9 µg mL^{-1}.

Table 2 Evaluation of calibration measurements with *MTC* in various supporting electrolytes. Survey of results together with basic detection characteristics

Solution #	Composition of the supporting electrolyte	Regression equation Correlation coefficient; LOD / LOQ (both in [μg mL^{-1}])	Linear range up to *ca*. (in [μg mL^{-1}])
1	0.1 mol L^{-1} H_2SO_4	I_p = 0.0306c + 0.0711 R = 0.9984; 0.23 / 0.50	c_{max} = 55
2	0.1 mol L^{-1} chloroacetate buffer; pH 3.5	I_p = 0.047c + 0.0904 R = 0.9986; 0.38 / 0.49	c_{max} = 31
3	0.1 mol L^{-1} acetate buffer; pH 4.53	I_p = 0.043c + 0.0689 R = 0.9990; 0.29 / 0.38	c_{max} = 32
4	0.1 mol L^{-1} citrate buffer; pH 6.62	I_p = 0.0456c + 0.121 R = 0.9984; 0.34 / 0.52	c_{max} = 39
5	0.1 mol L^{-1} phosphate buffer; pH 7.24	I_p = 0.0524c + 0.122 R = 0.9992; 0.31 / 0.43	c_{max} = 24
6	0.1 mol L^{-1} NaOH; pH *ca*. 13	--(the analyte could not be detected*)	

*Legend / Notes: I_P … peak height; LOD … limit of detection, LOQ … limit of quantification; * … for explanation, see text.*

It was found out that the increasing content of MeOH did not improve the resultant linearity so much; nevertheless, the presence of this solvent had revealed certain benefit. Namely, a percentage of about 10% (v/v) MeOH was found to give rise to the most satisfactory signal-to-noise ratio and hence, the solutions of 0.1 mol L^{-1} H_2SO_4 in 10% MeOH were used in the next experiments. Otherwise, the results of calibration measurements and their statistical evaluation from experimentation with the remaining MeOH-containing solutions are gathered in Table 3 in a similar arrangement like in the previous survey. Concerning the effect of MeOH, it should be yet noted that measurements in solutions with higher content of MeOH already suffered from unwanted shifts of the signal of interest to more positive potentials; i.e., towards the region with generally higher background.

Fig. 2 illustrates a typical cyclic voltammogram obtained by analysing the behaviour of *Methiocarb* with the BDDE and in mixed supporting medium of diluted sulphuric acid with MeOH (10%, v/v). A particularly well-developed curve - if one imagines the extremely high positive potential - documents clearly that the pesticide and its oxidation product represent totally irreversible system unable conversion between the oxidised and reduced forms.

Table 3 Evaluation of calibration measurements with *MTC* in 0.1 mol L^{-1} H_2SO_4 with different content of MeOH. Survey of results together with basic detection characteristics

Solution #	Composition of the supporting electrolyte	Regression equation Correlation coefficient; LOD / LOQ (both in [μg mL^{-1}])	Linear range up to *ca*. (in [μg mL^{-1}])
1	0.1 mol L^{-1} H_2SO_4	I_p = 0.0306c + 0.0711 R = 0.9984; 0.23 / 0.50	c_{max} = 55
2	0.1 mol L^{-1} chloroacetate buffer; pH 3.5	I_p = 0.0396c + 0.0480 R = 0.9997; 0.15 / 0.28	c_{max} = 55
3	0.1 mol L^{-1} acetate buffer; pH 4.53	I_p = 0.0349c + 0.0333 R = 0.9982; 0.20 / 0.45	c_{max} = 56
4	0.1 mol L^{-1} citrate buffer; pH 6.62	I_p = 0.0271c + 0.0497 R = 0.9999; 0.16 / 0.35	c_{max} = 63
5	0.1 mol L^{-1} phosphate buffer; pH 7.24	I_p = 0.0222c + 0.0214 R = 0.9999; 0.11 / 0.29	c_{max} = 64

Legend / Notes: I_P … peak height; LOD … limit of detection, LOQ … limit of quantification

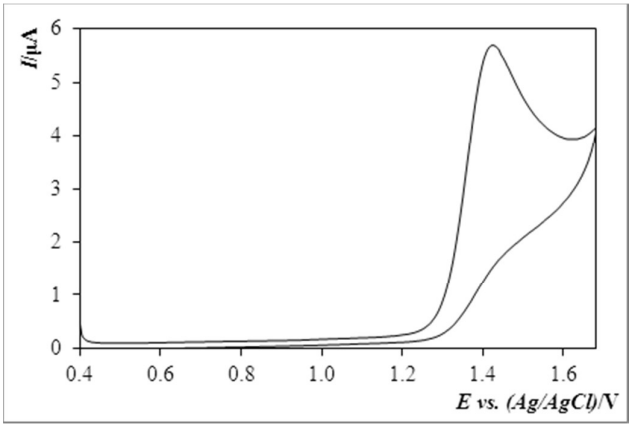


Fig. 2 Cyclic voltammogram of *Methiocarb* (*MTC*) in solution 0.1 mol L^{-1} H_2SO_4 + MeOH (10%, v/v) Exp. conditions: CV, E_{in} + 0.4 V, E_{fin} + 1.7 V vs. ref., scan rate: 40 mV s^{-1}, $c_{(MTC)}$ = 9.8 mg mL^{-1}.

The accuracy and precision of the determination of *Methiocarb* by DPV with BDDE was examined by means of the recovery (rate) measurements, when the sought concentration was quantified via the standard addition method with two successive aliquots.

By analysing five identical samples spiked with 2.94 μg mL^{-1} *MTC* one after the other, the concentration of the pesticide was found to be within an interval of 2.74 - 3.12 μg mL^{-1}, thus yielding the recovery of 93-106 %, which could be regarded as quite satisfactory result. One of such analyses is shown in Fig. 3, featuring typical DP-voltammograms.

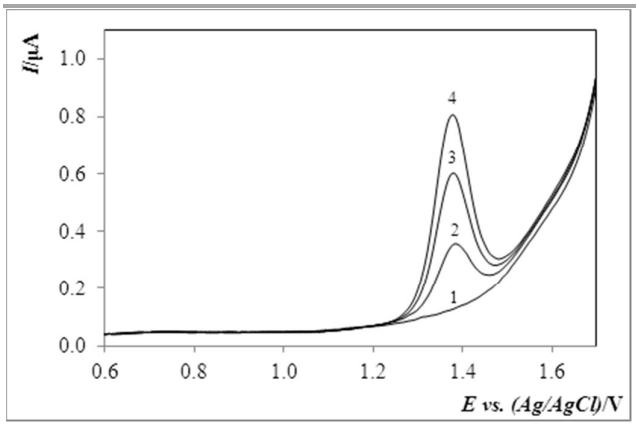


Fig. 3 DP-voltammograms of *MTC* in the supporting electrolyte (0.1 mol L^{-1} H_2SO_4 in MeOH (10%, v/v). Exp. conditions: DPV, E_{in} +0.4 V, E_{fin} +1.85 V, scan rate: 40 mV s^{-1}, Curve 1 … supporting electrolyte, 2 … *MTC* in model sample (c = 2.94 μg mL^{-1}), 3, 4 … additions of a 30 μL *MTC* standard solution (c_{MTC} = 0.98 mg mL^{-1}).

Practical Applicability of the Method: Determination of *MTC* and Observation of Its Activity in Dissolved Form

The method elaborated and characterised with respect to calibration and electroanalytical performance in the DPV regime was tested on the determination of *Methiocarb* (*MTC*) in two different experiments.

- The first assay has been focused on the determination of *MTC* in *Mesurol*® (*Mes*; AgroBio Opava, CZ), which is a product applied as effective slug killer in some agricultural localities and municipal gardens. In this case, of interest was mainly its controlled activity given by gradual dissolution of *MTC* in methanol. A chosen volume of the stock solution (made of 0.1045 g *Mes* in 25 mL MeOH) was pipetted into the above-optimised supporting electrolyte and the resultant mixture containing *ca*. 10 % MeOH then served for quantification of *MTC* in a series of analyses. These were performed consecutively within 75 hours, thus allowing us to monitor the slowly increasing content of *MTC* up to a limiting value – the maximal release of the active pesticide.

It was found that the concentration of *MTC* has increased up to 25 hours and afterwards, it exhibited a nearly steady-state character with almost constant content of the pesticide. This behavior was observed during next 50 hours. From the concentration found for the sample prepared from a take from a period after 25 hours (i.e., after maximal release), the content of *Methiocarb* in the commercial product could be determined as *ca*. 3 % (w/w) *MTC*. This was approximately 50 % higher compared to the average percertage of 2 % declared by the manufacturer or some dealers on the Internet; see e.g. paper[42]. Also, such a difference can be accepted, however, if one considers the low μg mL^{-1} concentration level of the substance to be analysed.

Fig. 4 shows typical sets of DP-voltammograms obtained by quantifying the *Methiocarb (MTC)* in the sample of *Mesurol*. In the figure, the upper image "A" shows the original responses for blank (base-line, 1), sample (2), and two subsequent standard additions (3, 4), whereas the lower set "B" depicts the same sequence after the base-line subtraction.

- The second experiment arranged to test the performance of newly proposed method was inspired by the occasionally reported ability of *Methiocarb* to suppress the undesirable growth of some zooplankton (during its gradual release from the preparation)[40]. Also, this assay has been made with *Mesurol*® product — which, in Czech Republic, is the only available source of *MTC* — added into natural water collected in a pond.

The proper test was made with a model medium containing 5.127 g *Mesurol* in 1000 mL (pond) water, when the respective suspension-like solution was stored in a fridge before being taken for voltammetric determination and actually analysed in the mixture with the supporting electrolyte (0.1 mol.l^{-1} H_2SO_4 in 10% MeOH).

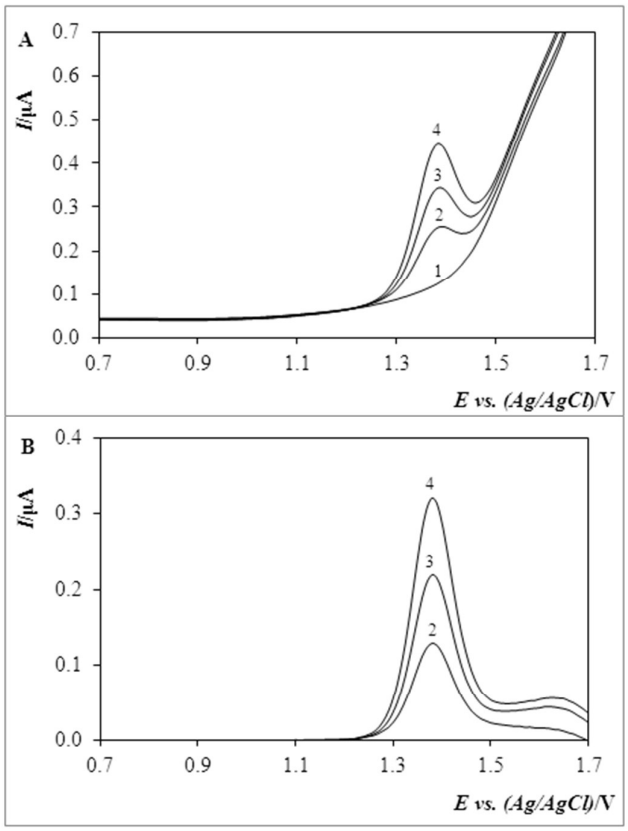


Fig. 4 DP-voltammograms obtained by analysing the methanolic solution of *Methiocarb* in *Mesurol*® commercial preparative before (A) and after (B) the subtraction of base-line (blank or the supporting electrolyte alone). Exp. con.: DPV, E_{in} +0.4 V, E_{fin} +1.7 V, scan rate: 40 mV s^{-1}, Curve 1 … 0.1 mol L^{-1} H_2SO_4 in MeOH (10%, v/v), 2 … *MTC* in model sample of *Mesurol* (200 µL solution containing 0.1045 g *MTC* in 25 mL MeOH), 3, 4 … two additions of 20 µL *MTC* standard solution with c_{MTC} = 0.98 mg mL^{-1}.

A plot in Fig. 5 then illustrates how the pesticide has behaved in the model sample from pond water, which could be monitored via the gradual increase of the content of *MTC* in the time course: after 2 days of storage, the respective analysis resulted in a content of 5.1 mg L^{-1} *MTC*, after 10 days increasing to 9.9 mg L^{-1} and after yet other 10 days attaining 11.4 mg L^{-1} *MTC*. When considering the overall shape of this curve, the lastly quoted number represents again the highest concentration of *MTC* during the period of observation. It can be anticipated according to the shape of the plot – that this concentration will gradually increase probably up to the total dissolution of the active pesticide.

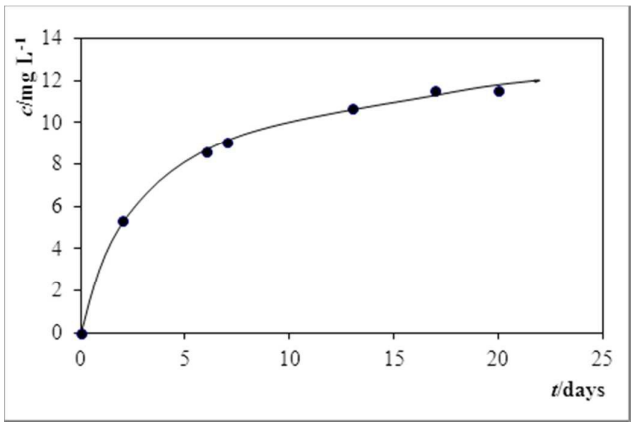


Fig. 5 Monitoring the activity of *MTC* in *Mesurol* via the time dependence of its gradually increasing solubility in model solution made of pond water.

Conclusions

In this article, a simple and rapid method for voltammetric determination of *Methiocarb* pesticide of the carbamate type has been proposed, developed, and tested on selected samples. Undoubtedly, a major benefit to this achievement lies in the choice of the working electrode – the BDDE, enabling us to perform the oxidative transformation of the analyte of interest at extremely high potentials of about +1.4 V vs. Ag/AgCl, which is a value, where a majority of common electrodes suffer from high background or even fail[36,40,43].

During the examination of the method in practical analysis, *Methiocarb* could be determined at the low µg mL^{-1} concentration level, which allowed us to follow the concentration variations during the controlled dissolution of the pesticide in aqueous media with real matrix; with respect to the determination itself in the presence of ca. 10% (v/v) MeOH. Such a monitoring seems to be very useful in environmental analysis, when one can observe the actual behaviour of this pesticide – either its slow and gradual dissolution in aquatic systems (to prolong the effectivity of its interaction with the target pest), or — oppositely — to monitor its biological bio-degradability in the environment.

Because these approaches may require the experimentation under field / outdoor conditions, simple and usually portable electrochemical devices are particularly convenient for this purpose; see *e.g.* discussion in paper[29] or the already proposed procedures for monitoring of some pesticides having demonstrated pretty well such a feasibility[44,45].

Acknowledgements

Financial support was provided by The Ministry of Education, Youth and Sports of the Czech Republic (Project No. **CZ.1.07/2.3.00/30.0021** "Strengthening of Research and Development Teams at the University of Pardubice").

References

1 H. P. Li, J. H. Li, G. C Li and J. F. Jen, *Talanta*, 2004, **63**, 547-553.
2 W. J. Hayes and E. R. Laws, *Handbook of pesticide toxicology (Classes of pesticides – vol. 3)*, Academic Press Inc., New York, 1991, pp. 1161-1163.
3 S. Ozben, B. Catalgol, S. Gezginci-Oktayoglu, A. Karatug, S. Bolkent and B. Alpertunga, *Toxicology and Industrial Health*, 2012, **29**, 60-71.
4 I. Altinok, E. Capkin, S. Karahan and M. Boran, *Environmental Toxicology and Pharmacology*, 2006, **22**, 20-26.
5 I. Altinok and E. Capkin, *Toxicologic Pathology*, 2007, **35**, 405-410.
6 J. Han, M. Park, J. H. Kim, A. Kim, M. Won, D. R. Lee, J. J. Ko, H. Yoon, S. H. Sim, K. Lee and J. Bae, *Journal of Applied Toxicology*, 2009, **29**, 446-451.
7 A. E. Essawy, N. E. Abdelmeguied, M. A. Radwan, S. S. Hamed and A. E. Hegazy, *Cell Biology and Toxicology*, 2009, **25**, 275-290.
8 G. Gras, C. Hasselman, C. Pellissier and R. Bruggers, *Bulletin of environmental contamination and toxicology*, 1981, **26**, 393-400.
9 V. Vlček and M. Pohanka, *Chem. Listy*, 2011, **105**, 908-912.
10 M. Pohanka, K. Musílek and K. Kuca, *Current Medicinal Chemistry*, 2009, **16**, 1790-1798.
11 R. Faina, J. Máchová, Z. Svobodová, H. Kroupová and O. Valentová, *Použití přípravku Diazinon 60 EC v rybníkářské praxi k tlumení nadměrného rozvoje hrubého dafniového zooplanktonu*, Jihočeská univerzita v Českých Budějovicích, Výzkumný ústav rybářský a hydrobiologický ve Vodňanech, 2007, pp. 18-19.
12 K. C. Ting and K. Peng, *J. of the Association of Official Anal. Chem.*, 1991, **74**, 991-998.
13 T. M. Primus, D. J. Kohler, M. Avery, P. Bolich, M. O. Way and J. J. Johnston, *J. Agric. Food Chem.*, 2001, **49**, 5706-5709.
14 V. A. Simon, K. S. Pearson and A. Taylor, *J. of Chromatography*, 1993, **643**, 317-320.
15 B. D. McGarvey, *J. of Chromatography*, 1993, **642**, 89-105.
16 C. Fernandez-Ramos, D. Satinsky and P. Solich, *Talanta*, 2014, **129**, 579-585.
17 J. F. Huertas-Perez and A. M. Garcia-Campana, *Anal. Chim. Acta*, 2008, **630**, 194-204.
18 F. Koc, Y. Yigit, Y. K. Das, Y. Gurel and C. Yaral, *J. of Food and Drug Analysis*, 2008, **16**, 39-45.
19 Z. H. Shi, J. D. Hu, Q. Li, S. L. Zhang, Y. H. Liang and H. Y. Zhang, *J. of Chromatography A*, 2014, **1355**, 219-227.
20 R. Carabias-Martinez, U. Garcia-Hermida, E. Rodriguez-Gonzalo and L. Ruano-Miguel, *J. of Separation Science*, 2005, **28**, 2130-2138.
21 M. J. Redondo, M. J. Ruiz, R. Boluda and G. Font, *J. of Chromatography A*, 1994, **678**, 375-379.
22 Q. Xia, H. W. Yuan, C. D. Wu, J. Zheng, S. Y. Zhang, C. H. Shen, B. Yi and R. Q. Zhou, *J. of Food Science*, 2014, **79**, 1854-1860.
23 W. M. Mo, H. L. He, X. M. Xu, B. F. Huang and Y. P. Ren, *Food Control*, 2014, **43**, 251-257.
24 B. Nagaraju and V. V. Rathnamma, *Toxicology Research*, 2014, **3**, 177-183.
25 T. L. Pham, T. H. Phan and T. D. Nguyen, *Soil and Sediment Contamination*, 2014, **23**, 339-352.
26 A. Placido, P. Paiga, D. H. Lopes, M. Correia and C. Delerue-Matos, *J. of Agrocultural and Food Chem.*, 2013, **61**, 325-331.
27 F. A. S. Oliveira, F. D. Madureira, R. P. Lopes, M. G. Ferreira, B. Soto-Blanco and M. M. Melo, *Quimica Nova*, 2014, **37**, 1699-1706.
28 J. Wang and D. Leung, *J. of AOAC Int.*, 2009, **92**, 279-301.
29 V. Guzsvány, Z. Papp, I. Švancara and K. Vytřas, *Electroanalysis of insecticides at carbon Paste electrodes with particular emphasis on selected neonicotinoid derivatives; in: Insecticides – Advances in Integrated Pest Management (Perveen F., Ed.), Chapter 24*, INTECH / Open Acces Publ., Rijeka (CRO), 2012, pp. 541-578.
30 E. Khaled and H. Y. Aboul-Eneim, *Pesticides; in: Environmental Analysis by Electrochemical Sensors and Biosensors, Volume 2: Applications (Moretto L.M. and Kalcher K., Eds.); Chapter 13*, Springer, New York, 2015, pp. 981-1020.
31 G. E. Batley and B. K. Afgan, *J. Electroanal. Chem.*, 1981, **125**, 437-445.
32 Y. Ni, P. Qiu and S. Kokot, *Anal. Chim. Acta*, 2005, **537**, 321-330.
33 R. Inam and C. Bilgin, *J. App. Electrochem.*, 2013, **43**, 425-432.
34 T. N. Rao, B.-H. Loo, B. V. Sarada, C. Terashima and A. Fujishima, *Anal. Chem.*, 2002, **74**, 1578-1583.
35 A. Fujishima, Y. Einaga, T. N. Rao, D. A. Tryk, *Diamond Electrochemistry*, BKC Press, Tokyo (Japan), 2005.
36 R. G. Compton, J. S. Foord and F. Marken, *Electroanalysis*, 2003, **15**, 1349-1363.
37 S. E. Jones Ward and R. G. Compton, *Current Analytical Chemistry*, 2008, **4**, 170-176.
38 L. Bandžuchová, Ľ. Švorc, M. Vojs, M. Marton, P. Michniak and J. Chýlková, *Int. J. of Environmental Anal. Chem.*, 2014, **94**, 943-953.
39 L. Janíková-Bandžuchová, R. Šelešovská, K. Schwarzová-Pecková and J. Chýlková, *Electrochimica Acta*, 2015, **154**, 421-429.
40 J. Musilová, J. Barek and K. Pecková, *Chemické listy*, 2009, **103**, 469-478.
41 Anonymous: Tribology Statistical Software (Adstat). TriloByte, Pardubice, Czech Republic, 1995.
42 http://www.e-zahradka.cz/store/goods-AB01034-112-mesurol-schneckenkorn250-g.html; Accessed 23 March 2015.
43 R. N. Adams, *Electrochemistry at Solid Electrodes*, M. Dekker, New York (USA), 1969.
44 V. Guzsvány, M. Kádár, Zs. Papp, L. Bjelica, F. Gaál and K. Tóth, *Electroanalysis*, 2008, **20**, 291- 300.
45 V. Guzsvány, Zs. Papp, L. Bjelica and F. Gaál, Voltammetric monitoring of photocatalytic degradation of Imidacloprid, Nitenpyram and Acetamiprid neonicotinoid insecticides; in: Sensing in Electroanalysis, Vol. 3 (Vytřas K. and Kalcher K., Eds.), Univ. Pardubice Press, Pardubice (CZ), 2008, pp. 105-116.