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THE POTENTIOMETRIC SENSOR FOR DETERMINATION OF THIABENDAZOLE

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ABSTRACT

This paper reports the development of a potentiometric sensor sensitive to thiabendazole. It was established, a slightly soluble compound of composition $(TBZ)_3(PMo_{12}O_{40})_2$ is formed as a result of the interaction of the organic cation of thiabendazole with 12-molybdophosphoric acid (used as a counterion). This composition was used as an electrode-active substance in the synthesis of film polyvinyl chloride membranes of the potentiometric sensor. The obtained ionic associate $(TBZ)_3(PMo_{12}O_{40})_2$ meet the conditions of the basic requirement for the electrode-active substance of plasticized polyvinyl chloride membranes of the potentiometric sensors (poor water solubility and good solubility in organic solvents). Phthalic acid derivatives (dibutyl phthalate and dioctyl phthalate) and tricresyl phosphate were used as plasticizers of the solvent for the polyvinyl chloride membrane. The influence of various factors on developed sensor's electrode characteristics was investigated: the nature of the membrane-plasticizer of the membrane, the nature of the electrode-active substance, the quantitative content of the electrode-active substance in the membrane, the nature of the counterion, the pH of the investigated solution. The optimal conditions for using the developed potentiometric sensor were found. The sensor response time does not exceed 50 sec, and the membrane life (~ 65 days) allows to carry out the determination without replacement. Developed potentiometric sensor, sensitive to thiabendazole, can be used to develop a potentiometric method for determining the quantitative content of thiabendazole in various objects of industrial production at the level of 10^{-4} – 10^{-5} mol/l in a short period of time (5 - 10 min).

Keywords: thiabendazole, polyvinyl chloride membranes, 12-molybdophosphoric acid, electrode-active substance, direct potentiometry, ionic associate, potentiometric sensor.

1. INTRODUCTION

Thiabendazole is a surface conservant with low toxicity, which belongs to a group of benzimidazoles. It has a depressing effect on the growth and spread of bacteria and fungi that can provoke rotting processes. It can successfully fight unwanted microorganisms even in very small concentrations. Thiabendazole is the most commonly used in the food industry to protect outside the citrus and banana from rotting as conservation to save products for a longer-term. E233 is used as a fungicide, a pesticide and an antibacterial agent for the treatment of plants before and after harvesting in agriculture [1,2]. Thiabendazole is used as an additive-sterilizer during maturation of wine [3].

High-performance liquid chromatography [4], gas chromatography [5-8], UV [9] and mass spectrometry [10-12], micellar electrokinetic chromatography [13,14] and QuEChERS solid-phase extraction solid-phase extraction are used for analytical control of thiabendazole determination [15-17]. However, these methods require a lengthy and rather complex preparation of the sample using toxic solvents.

According to previous studies [18-30], direct potentiometry using sensors that are sensitive to organic cations and substances is simple, fast and sensitive method of determination. The purpose of this study was to develop a potentiometric sensor that would quickly and efficiently detect thiabendazole in various environmental objects and foods.

2. MATERIALS AND METHODS

2.1 Materials used in the work

The following reagents were used in this work:

- Thiabendazole (pharmacopoeial purity);
- 12-molybdophosphate acid, $H_3PMo_{12}O_{40}x26H_2O$ (analytical purity);
- sodium hydroxide (analytically pure);
- hydrochloric acid (conc.) (analytically pure);
- polymeric matrix was polyvinyl chloride (PVC), brand C-70 (chemically pure);
- the matrix solvent was cyclohexanone (CG), (analytically pure);
- electrode-active substance (EAS) was $(TBZ)_3(PMo_{12}O_{40})_2$;
- membrane solvent plasticizer EAS was dibutyl phthalate (DBP), dioctyl phthalate (DOP) and tricresyl phosphate (TKF), (chemically pure).

As the electrode-active substance was used ionic associate of the organic cation of thiabendazole with 12-molybdophosphate acid.

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2.2. Devices were used in work

An electrochemical cell was used for researches of a direct potentiometry:

Ag	AgCl, $KCl_{sat.}$	detectable solution	plasticized membrane	internal solution ($1,0 \cdot 10^{-3}$M thiabendazole)	$KCl_{sat.}$, AgCl	Ag

Figure-1. Electrochemical cell for direct potentiometry.

The galvanic cell consisted of a film potentiometric sensor (with an internal solution of $1.0 \cdot 10^{-3}$ M solution of the test substance and an internal electrode - Ag / AgCl wire in KCl sat.) and an EBL-1M31 silver chloride comparison electrode with a saturated KCl solution.

Potentiometric measurements were performed at room temperature using an I-130 ionomer.

The acidity of the solutions was adjusted with HCL and NaOH solutions. The acidity was controlled by a potentiometric glass electrode ESK-10601/4.

2.3. Method for synthesis of plasticized membrane

Plasticized polyvinyl chloride membranes were synthesized according to the recommendations [19,31]: the weighted sample 0.45 g of PVC was dissolved in 4.5 ml of cyclohexanone under weak heat in a water bath while stirring until it was completely dissolved. A solution in a range of 0.001–0.01 g EAS from1.1 ml membrane solvent-plasticizer (MD) from TCPh was prepared in a water bath and mixed thoroughly until it was completely dissolved. The individual solutions of the polymer matrix (PM) and the EAS solution were mixed in a glass, adding a solution of EAS to the PM solution to form a transparent homogeneous liquid mixture. After that the mixture was moved to a Petri dish with 50 mm in diameter. The elastic transparent film of plasticized polyvinyl chloride membrane with weak orange color was obtained after complete evaporation of the CH from the mixture. The film has been held on under the exhaust cabinet (3-4 days) at room temperature (18-20°C). Plasticized membranes were synthesized using a similar method, using as a membrane solvent-plasticizers DBPh and DOPh.

3. RESULTS AND DISCUSSIONS

The optimum value of the content of the electrode-active substance in the membrane is 10 mg using as a solvent-plasticizer - TKF was established in the investigations of the choice of the optimal composition of the potentiometric sensor (Figure-2). In this case, the slope value of the electrode function of the membrane of the developed sensor retains a constant value of 30 mV/pC, which corresponds to the standard Nernst slope for two-charged ions.

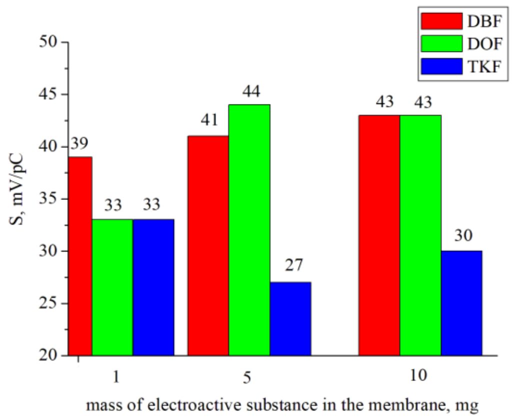

Figure-2. Dependence of the slope of the electrode function on the mass of the electrode-active substance in the membrane of the potentiometric sensor (plasticizer solvent are dibutyl phthalate, dioctyl phthalate, and tricresyl phosphate).

The effect of acidity of the test solution on the electrode characteristics of the membranes of the potentiometric sensor which is sensitive to thiabendazole was investigated using standard aqueous solutions of thiabendazole with concentrations from $1.0 \cdot 10^{-2} - 1.0 \cdot 10^{-6}$ mol/l (Figures 3 and 4).

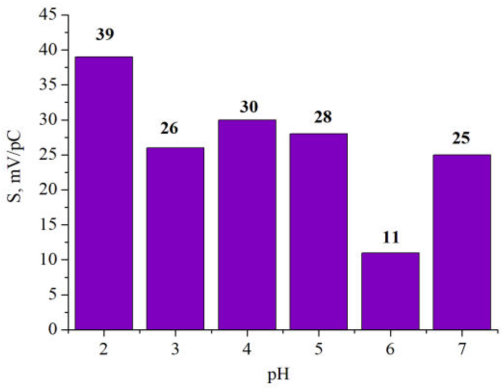

Figure-3. The influence of the acidity of the medium on the slope of the electrode function of the membrane sensor which is sensitive to thiabendazole.

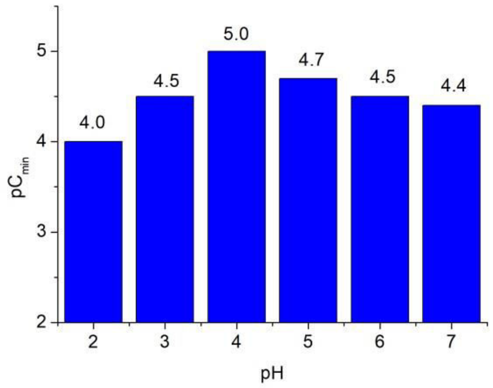

Figure-4. Effect of the medium acidity on the value of the determined minimum for the membrane of the sensor which is sensitive to thiabendazole.

The researches of the dependence of the electrochemical properties of the membrane of the potentiometric sensor on the solution pH show the slope of the calibration graphs in the pH range from 4.0 to 5.0 maintains a constant value of ~ 30 mV/pC, which is close to the theoretical value for two-charged ions. The optimum pH for the determination of thiabendazole with the potentiometric method is 4.0 because the membrane of the potentiometric sensor is most sensitive to the content of thiabendazole at the obtained acidity of the solution. The minimum determined concentration is 10^{-5} mol/l.

The researches of the influence of the nature of the plasticizer and the nature of the counterion on the slope of the electrode function of the membrane of the developed sensor (Figure-5) showed the experimentally determined value of the slope is close to the theoretical for two-charged ions when used TKF as solvent plasticizer for the membrane and 12-molybdophosphate acid was used as counterion. This acid forms stable ionic associates with thiabendazole which are characterized by low solubility in water and well-soluble in organic solvents.

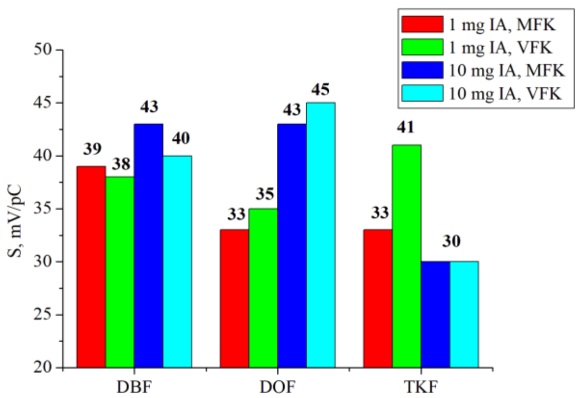

Figure-5. Dependence of the slope of the electrode function on the content of ionic associate in the membrane (pH=4.0).

The lowest concentrations (highest values of pC) were detected using TKF as a solvent in the research of the effect of the nature of the solvent-plasticizer on the values of the minimum determined concentration (Figure-6). The acidity of the test solution and the quantitative content of ionic associate in the membrane don't significantly affect this parameter.

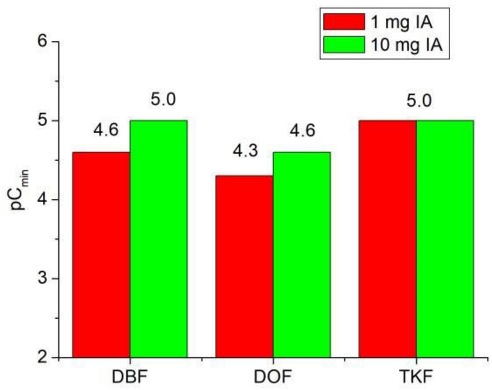

Figure-6. Dependence of the minimum determined concentration on the type of solvent (IA – $(TBZ)_3(PMo_{12}O_{40})_2$, pH=4.0).

Thus, the optimal operating conditions of the potentiometric sensor for thiabendazole were investigated (the interval of linearity of the dependence E = f (pC) from 10^{-6} to 10^{-2} mol/l with the slope of the electrode function S = 30 mV/pC, equal to the value of Nernst for two-charge cations): m_{IA} = 10.0 mg; membrane solvent plasticizer - TKF; pH = 4.0.

The dependence of the electrode potential of the developed potentiometric sensor on the concentration of thiabendazole in solution is shown in Figure-7.

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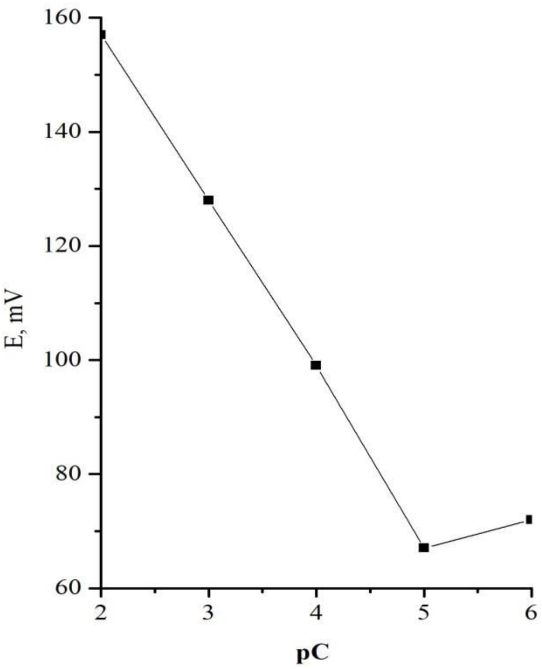

Figure-7. Dependence of the electrode potential on the logarithm of the concentration of thiabendazole (membrane containing 10.0 mg; pH = 4.0, MS is TKF).

It is experimentally established the response time of the developed potentiometric sensor is 120 - 180 sec at concentrations of $10^{-6} - 10^{-4}$ mol / l and decreases to 40 - 50 sec at concentrations of 10^{-3} - 10^{-2} mol/l. It is experimentally determined the optimum lifetime of the sensor is ~ 65 days when stored in a dry state.

4. CONCLUSIONS

a) It has been shown the synthesized ionic associate of composition $(TBZ)_3(PMo_{12}O_{40})_2$ can be used as an electrode-active substance in the development of a potentiometric sensor which is sensitive to thiabendazole.

b) A potentiometric sensor has been developed which can be used to determine the quantitative content of thiabendazole in various industrial products.

c) The choice of the optimal membrane composition of the potentiometric sensor and its working conditions were researched (the content of EAS in the membrane is 10.0 mg, the solvent is tricresyl phosphate, pH = 4.0).

d) The influence of various factors of the developed sensors (influence of the pH of the solution, the nature of the membrane solvent-plasticizer, the nature of the counterion, the content of the EAS in the membrane) on the characteristics of the electrode (minimum determined concentration, linearity interval and sensitivity S) have been investigated.

e) Experimentally determined the response time and optimal life time of the developed potentiometric sensor.

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