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Summary of PhD thesis:

„Square wave voltammetry as a tool in investigations of reaction mechanisms and quantitative determinations of pesticides”

The presented dissertation, described in the publication series, concerns the use of square wave voltammetry technique. Two main lines of research can be extracted. The first relates to the development of analytical methods for the determination of pesticides, the second - to explain the CE electrode mechanism and to study its kinetics based solely on the technique of square wave stripping voltammetry.

The objects of study in this series of publications were selected pesticides, such as acibenzolar S-methyl, clothianidin, diazinon and methidathion and application of the analytical capabilities of square wave stripping voltammetry. The tested compounds indicated the type and pH of the supporting electrolyte dependencies. The optimum values of the potential modulation parameters were selected, as well as the accumulation time and the accumulation potential. The recorded signals are the basis for voltammetric quantitative determinations of pesticides. Analytical methods for the determination of acibenzolar S-methyl, diazinon, methidathion and clothianidin have been developed. The prepared methods meet the criteria for validation in particular, when it comes to accuracy, precision, recovery.

Developed voltammetric procedures were used to study the tested compounds in spiked environmental samples. Prepared electroanalytical methods are fast, inexpensive, easy to make, and allow to monitor concentrations of these pesticides in the natural samples.

Cathodic stripping mechanism of sparingly soluble salt, adsorbed on the electrode surface and coupled with a homogenous chemical reaction of the reactive

ligand is considered for the first time in the square wave voltammetry. The most interesting feature is that the chemical reaction precedes (during the accumulation step) and follows-up (during the cathodic stripping) the electrode reaction. Therefore, during the cathodic stripping mode, the evolution of the square wave voltammetric response as a function of the rate of a chemical reaction is more complex than in the case of simple EC or CE mechanisms.

In the course of my experiments the investigated mechanism in the cathodic stripping mode have been characterized. The effect and the rate of the electrode reaction rate, as well as the rate of the chemical reaction of the generation and consumption of the reactive ligand have been also determined. Influence of the equilibrium position of a chemical reaction on the recorded voltammetric signal have been also pointed out.

Theoretical predictions have been supported with the experiments carried out for the real system, i.e. cathodic stripping mechanism of the oxidized working electrode material and the 6-mercaptopurine-9-D-ribose (MPR) complex, which is complicated with the complexation chemical reaction of MPR and nickel (II) ions. The developed characteristics made it possible to determine the standard rate constant of the electrode reaction and the chemical reaction rate constants. The latter allows to calculate the equilibrium dissociation constant of the $\text{Ni}^{2+}_{(\text{aq})}$ and a ligand MPR complex. The results were consistent with the literature data.