Detection of Copper-binding Pesticides using Copper Affinity Electrochemical Separation Electrospray Ionization Mass Spectrometry

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The detection and speciation of pesticides in environmental matrices is essential to insight into their role in the environment as well as it is one of current scopes of modern analytical chemistry. The interactions of metals (e.g., Ca, Cu, Mg, Zn) with pesticides have not been satisfactorily described up to now. Due to the fact that many pesticides are able to form relatively stable complexes with transition-metal ions, the metals present in soil may enter a plant together with pesticides present in soil [1, 2]. The analytical tools for the determination of total contents of the most frequent pesticides in biological samples have been satisfactorily developed [3]. However, these methods are inapplicable for detection of metal complexes with pesticides, because these methods include some kind of separation prior to the analytical measurement and the separation step may destroy the majority of these complexes.
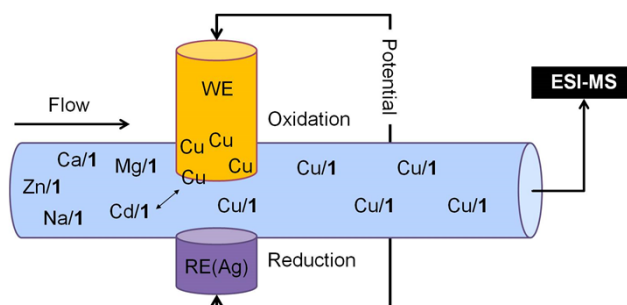
We developed a new method based on hyphenation of an electrochemical cell (**EC**) [4] with electrospray ionization mass spectrometer. It can be utilized for:
(i) detection of metal complexes with pesticides,
(ii) trace analysis of pesticides in environmental matrices,
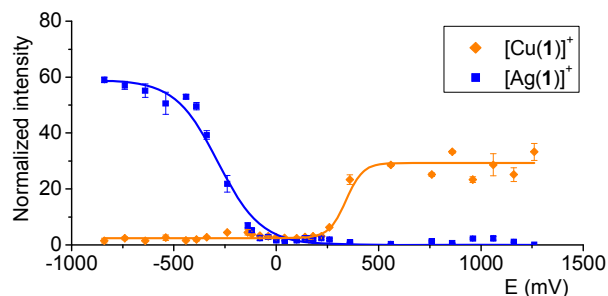(iii) stability and stoichiometry determination of such complexes.

Figure 1. Dependence of normalized intensities of the tebuconazole (denoted as **1**) complexes $[Cu(\mathbf{1})]^+$ and $[Ag(\mathbf{1})]^+$ on the inserted potential on the **EC**. The sample solution contained $2.5 \cdot 10^{-4}$ mol L^{-1} of **1**, in sodium acetate buffer ($2.5 \cdot 10^{-4}$ mol L^{-1}) mixed with methanol (1:1).
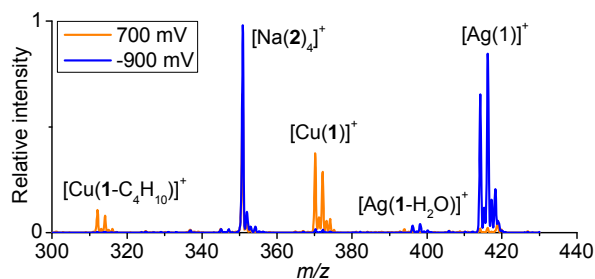

Figure 2. ESI-MS spectra of tebuconazole (denoted as **1**, $1.5 \cdot 10^{-4}$ mol L^{-1}) in sodium acetate (denoted as **2**)/acetic acid buffer ($2.5 \cdot 10^{-4}$ mol L^{-1}) mixture with methanol (1:1) measured in two potentials; positive +700 mV (orange) and negative -900 mV (blue).
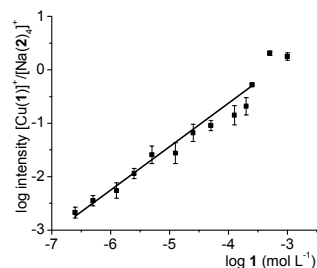

Figure 3. Calibration curve of tebuconazole (denoted as **1**) in $2.5 \cdot 10^{-4}$ mol L^{-1} sodium acetate (denoted as **2**)/acetic acid buffer mixture with methanol (1:1). The inserted potential on EC: +700 mV. The intensity is composed of intensity of $[Cu(\mathbf{1})]^+$ and of intensity of $[Cu(\mathbf{1}\text{-}C_4H_{10})]^+$.
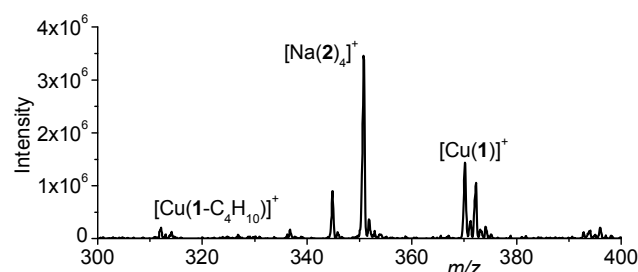

Figure 4. ESI-MS spectra of the soil solution spiked with tebuconazole (denoted as **1**); 25 % of the soil solution, 25 % of sodium acetate (denoted as **2**)/acetic acid buffer ($2.5 \cdot 10^{-4}$ mol L^{-1}) and 50 % methanol.

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