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Determination of flumioxazin residue in food samples through a sensitive fluorescent sensor based on click chemistry

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ABSTRACT

A sensitive and selective fluorescent sensor for flumioxazin was designed based on the formation of strong fluorescence compound (1,2,3-triazole compounds) via the reaction of the alkynyl group in flumioxazin with 3-azido-7-hydroxycoumarin, a weak-fluorescent compound, through the Cu^{+}-catalysed azide–alkyne cycloaddition (CuAAC) reaction. The fluorescence increase factor (represented by F/F_0) of the system exhibited a good linear relationship with the concentrations of flumioxazin in the range of 0.25–6.0 μg/L with a detection limit of 0.18 μg/L (S/N = 3). Also, the proposed fluorescent sensor demonstrated good selectivity for flumioxazin assay even in the presence of high concentration of other pesticides. Based on such high sensitivity and selectivity, the proposed fluorescent sensor has been applied to test the flumioxazin residue in some vegetable and water samples with satisfied results.

1. Introduction

As a well-known herbicide, flumioxazin has been efficiently used to remove weeds from the fields of soybean, peanut and orchards (Castro et al., 2008). However, the accumulation of flumioxazin in soil and crops will cause serious side effects (Poppell, Hayes, Mueller, & Agric, 2002), such as destroying the internal structure of the crops irreversibly. To ensure food safety, many countries, such as America, Canada and Japan, have set the maximum residue limit (MRL) of flumioxazin in some food as low as 0.02 ppm. So it is necessary to establish sensitive methods for flumioxazin determination.

The most widely used detection methods for flumioxazin are based on gas chromatography–mass spectrometry (GC–MS) (Jason & William, 2004) and liquid chromatography (Alder, Greulich, & Vieth, 2006). Though such methods have shown high sensitivity, expensive equipments are needed. Thus, it is necessary to develop a sensitive but simple method to examine the flumioxazin residue in food samples.

Click chemistry has drawn great attentions in the field of analytical chemistry in recent years because of its high efficiency and good selectivity. As one of the most widely used click chemistry reactions, the Cu^{+} catalysed alkyne–azide cycloaddition (CuAAC) (Kolb, Finn, & Sharpless, 2001) reaction has been successfully used to produce a highly fluorescent triazole complex through ligating the nonfluorescent 3-azidocoumarins and terminal alkynes (Sivakumar et al., 2004). Based on this reaction, many sensitive biosensors for different targets have been developed. For example, a sensitive signal-off fluorescent biosensor for histidine that was designed based on the fact that histidine can bind with Cu^{2+} and inhibit the CuAAC (Qiu, Miao, et al., 2013). Qiu et al. designed a fluorescent sensor for DNA sequence by taking advantages of copper nanoparticles (CuNPs) selectively formed on double stranded (ds) DNA template and CuAAC between 3-azido-7-hydroxycoumarin and propargyl alcohol (Qiu, Li, et al., 2013). Since flumioxazin has alkynyl groups that can react with azide through the CuAAC reaction, a colorimetric sensor for flumioxazin determination based on click chemistry has been proposed in an early study (Xie et al., 2013). Unfortunately, application of such sensor is inconvenient because of its complex reaction procedures and high incubation temperature.

Fluorescence determination owns the character of high sensitivity and simple equipment. The nonfluorescent 3-azidocoumarins can be ligated with the terminal alkyne group of flumioxazin to produce a highly fluorescent complex through the CuAAC reaction, the enhanced fluorescent intensity has a relationship with flumioxazin concentration, based on which, a simple and sensitive fluorescence sensor for flumioxazin can be developed. The proposed sensor has been applied to detect the flumioxazin residue in some vegetable and water samples with satisfied results.

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2. Materials and methods

2.1. Reagents and apparatus

Sodium ascorbate, $CuSO_4 \cdot 5H_2O$, 2,4-dihydroxy benzaldehyde, N-acetylglycine, anhydrous sodium acetate, acetic anhydride, and sodium azide were obtained from Alfa Aesar China (Tianjin) Co., Ltd. Double-distilled water was used throughout the whole process. Unless otherwise stated, all reagents were of analytical reagent grade and were used without further purification. 3-Azide-7-hydroxycoumarin was synthesised according to the literature (Zhou, Wang, Zhang, & Jiang, 2008). Flumioxazin was obtained from Dr. Ehrenstorfer GmbH laboratory.

Cary Eclipse Fluorescence Spectrophotometer (Varian Corporation, USA) was used for the measurements. The apparatus parameters were set as follows: λ_{ex} = 395 nm (slit 10 nm), λ_{em} = 400–600 nm (slit 10 nm).

2.2. Fluorescence spectroscopic measurements

To prepare the fluorescent sensor, 3-azido-7-hydroxycoumarin, flumioxazin and $CuSO_4$ were added to the phosphate buffer saline (PBS) solution (0.01 M, pH = 7.0). Then, sodium ascorbate was added to the above solution. The whole solution was subsequently incubated for 2 h at room temperature to form fluorescent 1,2,3-triazole compounds. The fluorescence emission spectra were collected at the excitation wavelength of 395 nm in PBS buffer solution (0.01 M, pH = 7.0). The fluorescence increase factor (F/F_0) was used for quantitative analysis, where F_0 and F represented the fluorescence intensity before and after the addition of flumioxazin, respectively. All the measurements were repeated five times and the standard deviation was calculated as the error analysis.

2.3. Sample preparation

The apple, garlic, soybean, peanut and strawberry samples were purchased from the local market and cut into small pieces. The tap water was taken directly in the laboratory and the river water was taken from the Minjiang River near Fuzhou University Yishan campus. 1 g samples were soaked in 0.010 L acetone and then centrifuged, the supernate of the samples was subjected to detection by the proposed method. For the apple, garlic, soybean, peanut and strawberry samples, 20 μL of the supernate was taken directly to be detected in PBS buffer solution (200 μL, 0.01 M, pH = 7.0). But for the tap water and the river water, the samples were flitted and diluted for 10 times first, then 20 μL of the diluted solution was taken to be detected in PBS buffer solution (200 μL, 0.01 M, pH = 7.0).

3. Results and discussion

3.1. Principle of the fluorescent sensor for flumioxazin

The principle of the fluorescent sensor is shown in Fig. 1A. The mixed solution of 3-azido-7-hydroxycoumarin and flumioxazin give off weak fluorescence signal. However, at the presence of sodium ascorbate (SA), Cu^{2+} can be reduced to Cu^{+}, which in turn catalyses the reaction between 3-azido-7-hydroxycoumarin and the alkynyl group of flumioxazin to form 1,2,3-triazole compounds, which give off strong fluorescence signal (Sivakumar et al., 2004). The F/F_0 has a linear relationship with the flumioxazin concentration and based on which, a sensitive fluorescent sensor for flumioxazin detection can be developed.

A simple experiment has been performed to verify our protocol. As shown in Fig. 1B, the individual solutions of 3-azido-7-hydroxycoumarin or flumioxazin give off weak fluorescence signals (column 1 and 2). No fluorescence change can be detected if SA

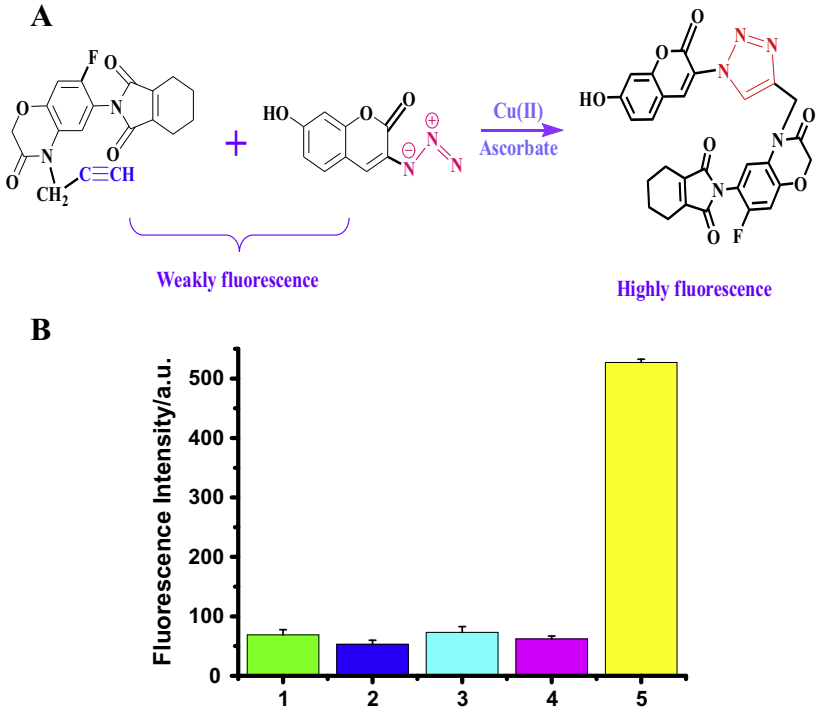

Fig. 1. (A) The principle of the proposed sensor. (B) The fluorescence of different solutions: (1) 3-azide-7-hydroxycoumarin; (2) flumioxazin; (3) 3-azide-7-hydroxycoumarin + Cu^{2+} + SA; (4) flumioxazin + Cu^{2+} + SA; (5) 3-azide-7-hydroxycoumarin + Cu^{2+} + SA + flumioxazin.