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Determination of carbendazim and metiram pesticides residues in reapeseed and peanut oils by fluorescence spectrophotometry

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ABSTRACT

Fluorescence spectrophotometry was applied to the determination of pesticide residue (carbendazim and metiram) in edible oil (rapeseed oil and peanut oil). Based on the fluorescence spectra of the oil–pesticide mixture, the prediction models between fluorescence intensity and pesticide content can be obtained. Functional relationship were found between fluorescence intensity and concentration of pesticide in the mixture and the correlation coefficient were greater than 0.99. We can calculate the detection limit is 7.07×10^{-4} mg/mL for rapeseed oil and 9.28×10^{-4} mg/mL for peanut oil, respectively. The prediction experiments show that the percent recovery range from 92.5% to 108.2%. It was verified that the fluorescence spectrophotometry method in this paper was feasible to detect the pesticide residues in edible oil. This study provides a new way for the detection of pesticide residues.

1. Introduction

Carbendazim is a wide-range bactericide, making influence on the diffusion of cells and exerting an effect in killing bacteria by interfering the formation of pathogen during mitosis, which plays a role in prevention of disease caused - by fungi on multiple kinds of crops [1]. Metiram, as a kind of protective fungicide which can prevent pathogen spores from germinating, suppress pathogen germ tube from growing, and by which cut off the way that pathogen may infect plant tissue, exerts an good effect on preventing all kinds of disease caused by oomycetes fungi [2]. Safety management of pesticides and food safety issues have been of concern to the international community. Widespread use of pesticide in agricultural production leads to excessive pesticide residues. Pesticide residue problems have become increasingly prominent and caused widespread concern around the world. People usually focus on the harm of environment or agricultural products, while ignoring the detection of pesticide residues in agro-processing products, for example a variety of juice or edible oil that are commonly used in daily life [3]. This leads to critical pesticide residue problem that can cause more danger to people's life. Therefore, an accuracy quantificational method for the detection of pesticide residue in agro-processing products is needed.

In recent years, a variety of edible oil quality and safety issues have become the focus of public attention, for example, quality and anti-adulteration control of vegetable oil [4], detection of genetically modified soybean in crude

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soybean oil [5], etc. The long-term intake of poor quality edible oil will cause great harm to human body, such as cell dysfunction, developmental disorders, and colitis [6]. It is very important to provide impartial, accurate and fast detection method of edible oil in order to create an environment that promotes fairness and efficiency in edible oil marketing system and to guard against deceptive and fraudulent practices affecting the movement and price of edible oil.

The effective detection of pesticide residues is of great value for human health. At present, methods of pesticide residues detection mainly include high performance liquid chromatography [7,8], gas chromatography [9], liquid chromatography–mass spectrometry [10,11], gas chromatography–mass spectrometry [12], enzyme immunoassay [13], biosensor technology [14] and spectrophotometry [15], etc. There are two reasons for the difficulty of pesticide residue detection. One is the wide varieties and complex composition of the pesticide, another is the detection requirements of trace analysis [16]. The demerits of these existing measurements lie in high cost and time consuming. Therefore, the exploration and development of new detection technologies has important significance for the study of food safety.

Fluorescence spectroscopy is a good method for the analysis of material composition and molecular structure [17]. This technique has been extensively investigated during the last decades because of the high sensitivity and nondestructive measurement [18]. Fluorescence spectroscopy can not only reflect the molecular structure and electronic state, but also the interaction information of the optical molecules and around molecules [19]. The technology has been widely used in industry, agriculture, environmental protection, mineral resources and other fields [20,21].

Based on fluorescence spectrophotometry, pesticide residues in edible oil was determined in this paper. According to the optical properties of the pesticide, the best measuring wavelength was selected. The standard curve could be obtained through the fluorescence spectrum measurement of the pesticide–oil mixture. The percent recovery experiment was carried on here to verify the measurement accuracy of this method. Measurement results show that the method of fluorescence spectrophotometry can be effectively realized the quantitative analysis of pesticide residues in edible oil with high accuracy and credibility.

2. Experimental

2.1. Instruments and samples

The fluorescence spectrum was recorded using a RF5301 spectrophotometer (Shimadzu, Japan) equipped with a Xenon lamp source, excitation and emission monochromators and a front-face sample-cell holder. Measurements were carried out using cuvettes. The instrumental settings were: the sampling interval is 0.5 nm, the slit width is 3.0 nm, the scanning wavelength ranges from 220 nm to 700 nm. All the absorption spectra were performed on a UV-3600 UV–VIS spectrophotometer (Shimadzu, Japan).

Rapeseed oil and peanut oil were purchased from large supermarket (Nanjing China). Carbendazim, metiram and carbon tetrachloride were obtained from Jiangsu Provincial Academy of Agricultural Sciences (Nanjing, China). The formula of carbendazim and metiram are shown in Fig. 1. Fig. 1a is the formula of carbendazim, Fig. 1b is the formula of metiram.

2.2. Experiment method

The standard liquid of pesticide (carbendazim and metiram) with appropriate concentration of 0.8 mg/mL (4×10^{-3} mol/L) and 0.35 mg/mL (4×10^{-4} mol/L) respectively was obtained by titrating with carbon tetrachloride. The fluorescence spectrum of the standard liquid was obtained using RF5301. Then the edible oil (rapeseed oil or peanut oil) was diluted by carbon tetrachloride with the volume ratio of 1:20 and the fluorescence spectrums were recorded. The two kinds of edible oil (3 mL) were taken using cuvette respectively and the pesticide standard solution was mixed with the edible oil by successive addition from 0.1 to 1.0 mL. After sufficiently stirred, the edible oil and drug solution should be mixed well and their fluorescence spectrums were obtained with a certain excitation wavelength.

The UV3600 spectrophotometer is used to scan the absorption spectrum of the carbendazim and metiram standard liquid. It can be seen from Fig. 2 that the strongest absorption peaks of carbendazim and metiram standard liquid are at 295 nm and 235 nm, respectively. Based on the results, the selected excitation wavelength of carbendazim is $\lambda_{ex} = 295$ nm and metiram is $\lambda_{ex} = 235$ nm. Fig. 3 shows the representative standard curves of fluorescence spectrum about standard pesticide solution and edible oil. The abscissa indicates the emission wavelength while the ordinate indicates fluorescence intensity. In addition, the curve of (a) and (c) represent the fluorescence spectra of rapeseed oil and carbendazim with the excitation wavelength of 295 nm, respectively. The curve of (b) and (d) represent the fluorescence spectra of peanut oil and metiram with the excitation wavelength of 235 nm, respectively. As can be seen that carbendazim has a strong fluorescence peak at 320 nm and metiram has two strong fluorescence peaks at 375 nm and 468 nm, respectively. The fluorescence intensity at 468 nm is greater than that in 375 nm. Meanwhile, there is no characteristic peaks of rapeseed oil and peanut oil in this situation. According to

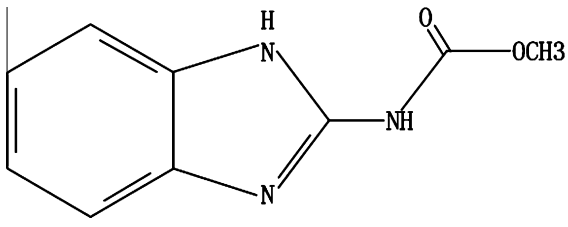

Fig. 1a. The formula of carbendazim.