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A convenient method for determination of malathion based on the resonance Rayleigh scattering enhancement

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ABSTRACT

A convenient method for determination of malathion (Mala) based on resonance Rayleigh scattering (RRS) enhancement of L-Tryptophan (L-Try)-Pd(II)-Mala system was proposed in this paper. The interaction between L-Try, Pd(II) and malathion in the system was investigated by fluorescence, RRS and UV−Vis absorption spectroscopy. In the optimum conditions, the RRS intensity of L-Try-Pd(II)-Mala system had a remarkable enhancement because the hydrolysis products of malathion would interact with Pd(II) and L-Try each other formed new complexes, which enhanced intensity was directly proportional to the malathion concentration within a certain range. Based on the RRS enhancement of L-Try-Pd(II) system by Mala, a novel, convenient and specific method for Mala determination was developed. To our knowledge, the method is the first RRS method for determination of Mala was reported. The detection limit for Mala was 6.7 ng/mL and the quantitative determination range was 0.06−0.6 μg/mL. The influence of coexisting substances on RRS was also investigated, and the RRS method exhibited good anti-interference ability. The new analytical method has been applied to determine of malathion in real samples with satisfactory results.

1. Introduction

Pesticides have played an important role in agricultural production and in the control of many disease vectors in the area of public health. The worldwide use of pesticides increased tremendously since the 1960s [1,2]. Then, their contaminant residue have reported in food and environmental samples, and they have high toxicity to organisms include human [3]. Especially, the use of organophosphorus compounds (OPPs) in pesticides for agricultural production is widely increasing throughout the word [4]. OPPs are a class of chemicals i.e. organic esters of phosphoric acid, thiophosphoric acid and other phosphoric acids. Because of their high insecticidal activity, OPPs have widely been used in agriculture production as insecticides and herbicides as the replacement for persistent organochlorinated pesticides [5,6].

Malathion (Mala) is a non-systemic, wide-spectrum OPPs. It was developed for the first time in 1950 [7] and was first registered for use in 1956 in United States by the United States Department of Agriculture [1]. And it is used as insecticides for insert control on corn, maize, fruits and vegetables to reduce crop losses and to increase the production. Everything has two sides, malathion was benefit for agriculture production, but it could cause some problems for human. It has reported [8], toxic symptoms resulting from malathion to human, include breathing problems, headache, dizziness, it could even produce fetal poisoning while high exposure. The acute toxicity of malathion is it could inhibit the acetylcholinesterase activity, decrease the production of choline. The cholinergic manifestations can finally cause respiratory paralysis and death [9–11]. The health based value for malathion in drinking water, set by Ministry of Health P.R.China (MHC) is 0.25 μg/mL [12]. The maximum residual level (MRL) of Mala in fruits such as orange and apple was limited at 2 μg/kg, the MRL in other crops such as corn and tea was limited at 0.5 μg/kg [13]. Hence it is important and necessary to determinate the residues of malathion in water and other environmental samples to protect the human and

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environment from its hazardous effect.

Many methods have been developed for the determination of malathion in the past few years. The most widely used methods are: high-performance liquid chromatography (HPLC) [14,15], gas chromatography (GC) [16,17], Raman spectrometry [7], Fluorescence assay [4,18], UV spectrophotometry [19,20], electro and electro luminescence methods [21–23]. Although these methods are accurate and selective, they are very expensive, involve time-consuming pretreatments and require relatively expensive instrumentation and highly skilled technicians. For this reason, there are increasing demands to develop a convenient, highly sensitive and effective assay for determination of malathion in real environmental samples. Resonance Rayleigh scattering (RRS) has attracted great attention due to its simplicity and high sensitivity. RRS is a special elastic scattering and has a special synchronous fluorescence of $\Delta\lambda = 0$ (i.e., $\lambda ex = \lambda em$), which occurs when the wavelength of the rayleigh scattering spectral band is located at or closed to the molecular absorption band [24]. It has been successfully applied to the analysis of some substance [25,26]. To our knowledge, the application of RRS assay for determination of malathion has not been reported.

Herein, a convenient RRS assay for determination of malathion was proposed based on the RRS of L-Tryptophan (L-Try) in the presence of palladium chloride (Pd(II)) significantly enhanced. L-try has strong fluorescence but RRS is weak. The fluorescence of L-Try could be quenched by Pd(II) but the RRS had no changes under optimum conditions. Interestingly, the RRS of L-Try-Pd(II) system could be enhanced remarkably while introducing malathion into and the fluorescence could be recovered. Based on the changes of RRS, the RRS assay for determination of malathion was developed. The optimum reactions and the influencing factors have also been examined. Finally, the method has been applied to determination of malathion in real samples, and satisfactory results were obtained. The mechanism of the proposed reaction was also discussed.

2. Experimental

2.1. Apparatus

FS5 fluorescence spectrometer (Edinburgh Instruments, Edinburgh, Scotland) with excitation and emission slit width of 5 nm was used to record resonance Rayleigh scattering (RRS) spectra and the fluorescence (FL) spectra. Shimadzu UV-2700 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) was used to record the absorption spectra. pHS-3C-02 m (Shanghai San-Xin Instrumentation Inc, Shanghai, China) was used to measure the pH value of the solution.

2.2. Chemical reagents

All chemical reagents were used as purchased with no additional purification. The standard sample of herbicides (Malathion, Glyphosate, Dichlorrop, Fenobucarb, Metorlachlor, Dipeterex) and the amino acids (Tryptophan, Cysteine, Histidine, Arginine, Serine and etc.) were purchased from J&K Scientific (China). The metal salts ($PdCl_2$, $Cu(NO_3)_2$, Na_2SO_4, NaCl, and etc.) and other chemicals were purchased from Sinopharm Chemical Reagent Co.(China). $PdCl_2$ was dissolved with HCl and diluted with doubly distilled (DD) water (HCl:DD = 1:9). Other chemical reagents were dissolved and diluted with doubly distilled water.

BR buffer solutions with different pH values were prepared by dissolving different amounts of H_3PO_4, H_3BO_3, CH_3COOH and NaOH in DD water. The working solution of L/D-Try, $PdCl_2$ and Mala were 1.0×10^{-3} mol L^{-1}, 1.0×10^{-3} mol L^{-1} and 40 μg/mL, respectively.

2.3. General procedure

First, 500 μL BR buffer solution, 100 μL 1.0×10^{-3} mol L^{-1} L/D-Try and 50 μL 1.0×10^{-3} mol L^{-1} Pd(II) were added into a 10 mL calibrated test tube. Then, different concentrations of Mala were introduced into the above prepared solution, diluted with DD water to the mark, and mixed thoroughly with gentle shaking. The mixed solution was allowed to react for about 25 min at room temperature. Finally, the FL spectra and RRS spectra were recorded. Where F_0 and F standed for the fluorescence intensity of reagent blank and complexes respectively, $\Delta FL = F\text{-}F_0$, while ΔRRS standed for RRS intensity enhanced degree.

3. Results and discussion

3.1. RRS and fluorescence spectra

The RRS spectra was shown in Fig. 1. The RRS intensity of L-Try-Pd(II) was very weak, however when introduced Mala into L-Try-Pd(II) system, the RRS intensity was enhanced greatly and altered. The maximum RRS peak was observed at 325 nm. And the enhanced intensity were proportional to concentrations of Mala. Therefore, based on the RRS intensity enhanced, RRS method for

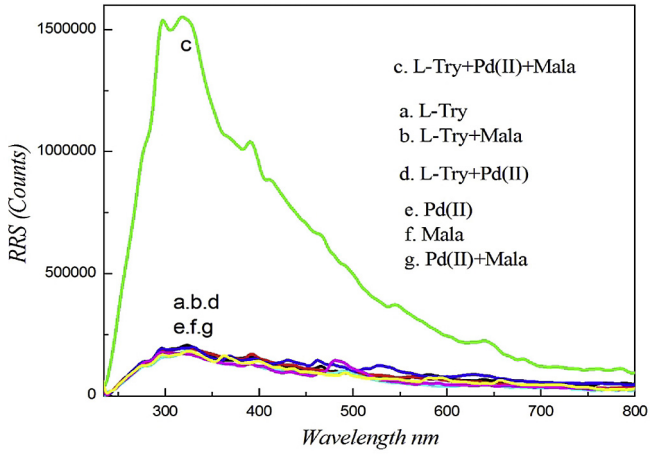

Fig. 1. The RRS spectrum. L-Try: 1.0×10^{-5} mol/L, Pd(II): 0.5×10^{-5} mol/L, Mala: 1.2 μg/mL in pH 4.35 BR buffer solution, respectively.

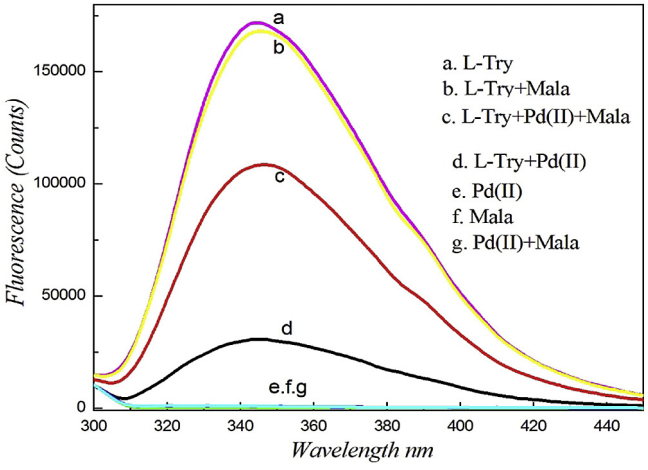

Fig. 2. The fluorescence spectrum. L-Try: 1.0×10^{-5} mol/L, Pd(II): 0.5×10^{-5} mol/L, Mala: 1.2 μg/mL in pH 4.35 BR buffer solution, respectively.