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# Study on the interaction between albendazole and eosin Y by fluorescence, resonance Rayleigh scattering and frequency doubling scattering spectra and their analytical applications

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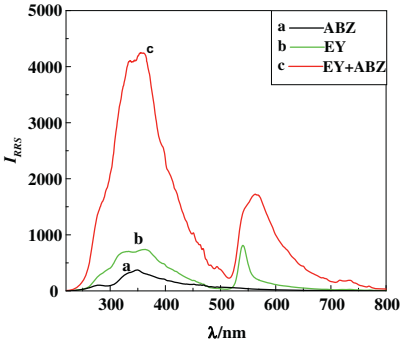
## HIGHLIGHTS

- A convenient, rapid and sensitive RRS method has been developed for albendazole detection.
- The RRS method was applied successfully to the determination of albendazole in capsules and urine.
- The detection limit for albendazole reached nanogram level.
- The possible mechanism for the RRS enhancement of EY–ABZ system was discussed.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In pH 3.25–3.35 Britton–Robinson (BR) buffer solution, albendazole (ABZ) could react with eosin Y (EY) to form a 1:1 ion-association complex, which not only results in the quenching of fluorescence, but also resulted in the great enhancement of resonance Rayleigh scattering (RRS) and frequency doubling scattering (FDS). Furthermore, a new RRS spectrum will appear, and the maximum RRS wavelength was located at about 356 nm. The detection limit for ABZ were 21.51 ng $mL^{-1}$ for the fluorophotometry, 6.93 ng $mL^{-1}$ for the RRS method and 12.89 ng $mL^{-1}$ for the FDS method. Among them, the RRS method had the highest sensitivity. The experimental conditions were optimized and effects of coexisting substances were evaluated. Meanwhile, the influences of coexisting substances were tested. The methods have been successfully applied to the determination of ABZ in capsules and human urine samples. The composition and structure of the ion-association complex and the reaction mechanism were discussed.


## Introduction

Albendazole (ABZ), methyl-[(5-propylthio)-1H-benzimidazol-2-yl] cabamate (Fig. 1), is a broad-spectrum anthelmintic agent and is widely used for treatment of parasitic diseases and human helminthiasis [1–3]. ABZ is effective in the treatment of neurocysticercosis [4,5]. However the therapeutic response in echinococcosis is unpredictable due to poor bioavailability [6,7]. Therefore, it is significant that a new method for the determination of ABZ will be further researched and developed.

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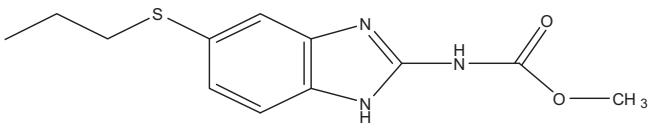

**Fig. 1.** Methyl-[(5-propylthio)-1H-benzimidazol-2-yl] cabamate.

Some methods such as high-performance liquid chromatography (HPLC) [8,9], electrochemical oxidation [10], liquid chromatography–tandem mass spectrometry (LC–MS–MS) [11], liquid chromatography (LC) [12] and spectrofluorimetry [13,14] were used for the determination of ABZ. Some methods need complicated pretreatment and operation (e.g. HPLC), and some need expensive apparatus and not applied to daily analysis (e.g. LC–MS–MS). Therefore, it is still a worthwhile subject to develop a highly sensitive, convenient and rapid method for determining the trace ABZ.

Resonance Rayleigh scattering (RRS), as a new analytical technique, has been successfully applied to the determination of macromolecules such as heparin [15–17], proteins [18–21] and nucleic acids [22–24] and also used for the determination of some trace inorganic ions [25–29], surfactants [30,31], drugs [32–38], organic compounds [39] and some physico-chemical parameters [40,41].

The effects of the reaction of EY and ABZ on the fluorescence, resonance Raleigh scattering and frequency doubling scattering spectra have been investigated in our experiment. Meanwhile, the optimum reactions, the influencing factors have also been examined. Moreover, the influences of coexisting substances were tested by RRS method and the results indicated that this method had a good selectivity. Therefore, this method could be satisfactorily applied to the determination of ABZ in capsules and human serum samples.

## Experimental

### *Apparatus*

A Hitachi F-2500 spectrofluorophotometer (Tokyo, Japan) was used for measuring the scattering intensities and recording the RRS and fluorescence spectra. The slits (EX/EM) were 5.0/5.0 nm for RRS and 10.0/10.0 nm for FDS and fluorescence; A UV-4100 spectrophotometer (Tianmei, Shanghai) was used for recording the absorption spectra. A pHS-3C pH meter (Shanghai, Precision & scientific instrument Co. LTD., China) was used for adjusting pH values.

### *Reagents*

Albendazole (ABZ) (National Institutes for Food and Drug Control): 0.0500 g of ABZ was weighed, dissolved in a 250 mL volumetric flask as stock solution (200 mg $L^{-1}$), and diluted to 20 μg $L^{-1}$ as working solution. The stock solution of eosin Y (Chengdu Kelong Chemical Reagent Plant) was $2.0 \times 10^{-3}$ mol $L^{-1}$, and then diluted 10 times with doubly distilled water to $2.0 \times 10^{-4}$ moL $L^{-1}$ as working solution. Britton–Robinson (BR) buffer solutions were prepared by the mixed acid (composed of 0.04 mol $L^{-1}$ $H_3PO_4$, HAc and $H_3BO_3$) and 0.2 mol $L^{-1}$ NaOH in suitable proportions, the pH values were adjusted by a pH meter. All reagents were analytical reagent grade (A.R.), and doubly distilled water was used throughout.

### *General procedure*

Into a 10 mL calibrated flask, were added 1.0 mL of pH 3.3 BR buffer solution, 1.2 mL of EY solution and appropriate amount of ABZ solution in turn. The mixture solution was diluted to the mark with doubly distilled water, shaken thoroughly. After 10 min, the RRS spectra of the system were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ ($\Delta\lambda = 0$) and the FDS intensity ($I_{FDS}$) of the system were recorded at $2\lambda_{em} = \lambda_{ex}$, respectively. The scattering intensities $I_{RRS}$ and $I_{FDS}$ for the reaction product and $I^0_{RRS}$ and $I^0_{FDS}$ for the reagent blank at their maximum wavelengths were measured, $\Delta I_{RRS} = I_{RRS} - I^0_{RRS}$ and $\Delta I_{FDS} = I_{FDS} - I^0_{FDS}$. Simultaneously, the spectra for fluorescence and absorption were recorded, respectively.

## Results and discussion

### *Fluorescence spectra*

The florescence spectra of EY–ABZ system are shown in Fig. 2. As shown in Fig. 2, ABZ itself does not exhibit fluorescence, but EY has strong fluorescence, its maximum excitation wavelength ($\lambda_{ex}$) and maximum emission wavelength ($\lambda_{em}$) is 522 nm and 548 nm in pH 3.3 BR buffer solution. When EY reacted with ABZ to form ion-association complexes, its fluorescence quenched strongly (Fig. 2) and the quenched intensity ($\Delta F$) was directly proportional to the concentration of ABZ in a certain range. Hence, it can be applied to the determination of ABZ.

### *RRS spectra*

The RRS spectra of EY–ABZ system are shown in Fig. 3. Fig. 3A shows that the RRS intensities of EY and ABZ were very weak under the measurement conditions. However, when EY was mixed with trace amounts of ABZ to form an ion-association complex, the RRS intensity was enhanced greatly. The maximum RRS peak was located at 356 nm, and the enhancement of RRS intensity for EY–ABZ system was proportional to the concentration of ABZ in a certain range. Fig. 3B shows the linear relationship between ABZ concentration and RRS intensities. So, the RRS method can be applied to the determination of ABZ.

### *FDS spectra*

In 220–800 nm wavelength range of the F-2500 spectrofluorophotometer, when the incident light ($\lambda_{ex}$) with longer wavelength (440–800 nm) gets across the solution, it can be seen that FDS appears at $\lambda_{em} = 1/2\ \lambda_{ex}$. By scanning every 10 nm with $\lambda_{ex}$ from 440 to 800 nm, the FDS scanning spectra (Fig. 4A) were obtained. It can be seen from Fig. 4A that: (1) the FDS intensities at different incident wavelength are different; (2) under experimental conditions, the FDS intensities of EY and ABZ are very weak, but the EY–ABZ association complex has strong FDS intensities. Their maximum scattering wavelength $\lambda_{em}/\lambda_{ex}$ appear at 395/790 nm. Fig. 4B shows that at the maximum wavelength of FDS, the scattering intensity of FDS is proportional to the concentration of ABZ in a certain range. Therefore, FDS method can be applied to determine ABZ.

### *Optimum conditions for the reaction*

#### *Effect of the acidity*

The influences of different buffer solution on RRS intensities were tested with HAc–NaAc, HCl–NaAc, BR and $C_6H_5O_7Na_3$–HCl. The results showed that BR was better than other buffer solutions and the optimum pH ranges for the determination of ABZ were 3.25–3.35 (Fig. 5). So, pH 3.3 was chosen as reaction acidity for the system and the appropriate amount was 1.0 mL.