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Resonance Rayleigh scattering, frequency doubling scattering and absorption spectrum of the interaction for mebendazole with 12-tungstophosphoric acid and its analytical applications

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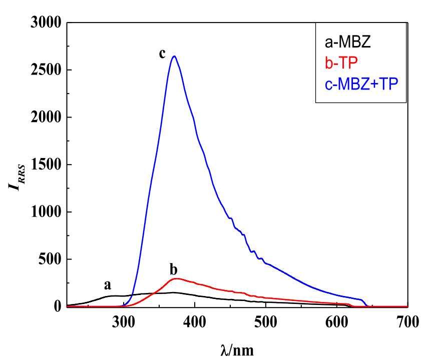
HIGHLIGHTS

- A novel method determining mebendazole (MBZ) was proposed.
- The detection limit for MBZ reached nanogram level.
- The possible mechanism for the RRS enhancement of TP-MBZ system was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction of mebendazole (MBZ) with12-tungstophosphoric acid (TP) has been investigated by using resonance Rayleigh scattering (RRS) and frequency doubling scattering (FDS) combining with absorption spectrum. In pH 1.0 HCl medium, MBZ reacted with TP to form 3:1 ion–association complex. As a result, not only the spectrum of absorption was changed, but also the intensities of RRS and FDS were enhanced greatly. The maximum RRS, FDS and absorption wavelengths are located at 372, 392 and 260 nm, respectively. The increments of scattering intensity (ΔI) and absorption (ΔA) are directly proportional to the concentrations of MBZ in certain ranges. The detection limits (3σ) of RRS, FDS and absorption are 0.56, 0.86 and 130.16 ng/mL, respectively. The sensitivity of RRS method is higher than FDS and absorption methods. The optimum conditions of RRS method and the influence factors were discussed in the paper, in addition, the structure of ion–association complex and the reaction mechanism were investigated. Based on the ion–association reaction and its spectral response, the rapid, simple and sensitive RRS method for the determination of MBZ has been developed.

Introduction

Mebendazole (MBZ) (Fig. 1) is a synthetic broad-spectrum anthelminthic drug [1] with potential antitumor activity [2] and high efficacy against common nematode parasites including Ascaris, threadworms, hookworms and whipworms in both human and animals [3–7]. Pharmacologically, MBZ is very stable [8], it has been widely used for its relatively poor absorption from the intestine and the low cost of this drug further enhance its therapeutic appeal. However deficiency of MBZ may cause the unwanted systemic effects. Therefore, it is significant that a new method for the determination of MBZ will be further researched and developed.

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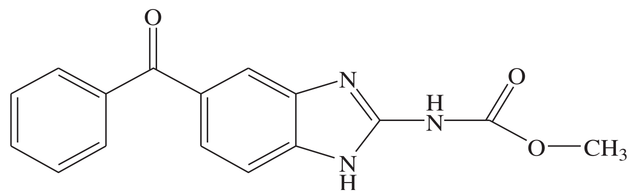

Fig. 1. Structure of mebendazole (methyl [(5-benzoyl-3H-benzoimidazol-2-yl)amino] formate).

So far, various methods were reported for the determination of MBZ such as titration techniques [9], spectrophotometry (SP) [10], infrared Spectroscopy [11], fluorescence (F) [12,13], high-performance liquid chromatography (HPLC) [14], high-performance liquid chromatography-reverse phase (RP-HPLC) [15], proton NMR [16], mass spectrometry [17], polarography [18] and phosphorescence [19]. Among them, Spectrophotometric methods have been applied in the determination of MBZ due to its simple and fast, but its sensitivities were not high enough for trace analysis. HPLC was very useful for the determination of trace MBZ in some complicated samples, but it needed complex pretreatments. Some other reported methods such as fluorescence and phosphorescence methods also have some deficiencies in the selectivity, simplicity and sensitivity. So, it is necessary to develop a highly selective, convenient, rapid and sensitive method for the determination of MBZ.

Resonance Rayleigh scattering (RRS) and frequency doubling scattering (FDS) have been paid more and more attention due to their simplicity and high sensitivity. At present, it has been successfully applied to the analysis of biomacromolecules such as proteins [20–22], heparin [23,24] and nucleic acids [25–28] and also used for the determination of some trace inorganic ions [29–32], surfactants [33,34], drugs [35–37], organic compounds [38,39]and some physico-chemical parameters [40–42].

Our experiment discovered that the RRS and FDS intensities of the MBZ solution were very weak, and the RRS peak was at 372 nm and the FDS peak appeared at 392 nm. However, in the mix system with strong acid medium, MBZ could react with 12-tungstophosphoric acid (TP) to form 3:1 ion–association complex, which could lead to the remarkable enhancement of RRS and FDS. These methods all could be developed through these experiment and applied to determine MBZ, and RRS method will be mainly discussed because the sensitivity of RRS was higher than FDS. Thus the optimum reactions, the influence of coexisting substances on RRS were investigated. In addition, the effects of formation of $[MBZ]_3[TP]$ to absorption spectra and RRS were invested and the mechanism for the enhancement of RRS were also discussed in paper.

Experimental

Apparatus

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

Reagents

Mebendazole (MBZ) (Shanghai Aladdin Chemical Reagent Company, China): 0.0250 g of MBZ was weighed, dissolved in a 250 mL volumetric flask as stock solution (0.1 mg/mL), and diluted to 20 μg/mL as working solution. 12-Tungstophosphoric acid (TP) was synthesized as previously described [43]. The stock solution of TP was 2.0×10^{-2} mol/L, and then diluted 10 times with doubly distilled water to 1.0×10^{-3} mol/L as working solution. All reagents were analytical reagent grade (A.R.), and doubly distilled water was used throughout.

General procedure

Suitable amounts of MBZ solution were placed in a 10 mL calibrated flask, followed by 1.0 mL of 1.0 mol/L HCl, 1.1 mL of 2.0×10^{-3} mol/L TP solution; finally, the mixture solution was diluted to the 10 mL with water and mixed thoroughly. After 10 min, the RRS spectra of the solution were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ ($\Delta\lambda = 0$) in the range of 220–800 nm, and then the frequency doubling scattering (FDS) spectra were recorded by scanning at $\lambda_{ex} = 2\lambda_{em}$ 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, $\Delta I_{RRS} = I_{RRS} = I^0_{RRS}$, $\Delta I_{FDS} = I_{FDS} = I^0_{FDS}$ Simultaneously, the absorption spectra were recorded.

Results and discussion

RRS spectra

The RRS spectra of MBZ-TP system are shown in Fig. 2. Fig. 2A shows that the RRS intensities of MBZ and TP were very weak under the measurement conditions. However, when TP was mixed with trace amounts of MBZ to form an ion–association complex, the RRS intensity was enhanced greatly. The maximum RRS peak was located at 372 nm, and the enhancement of RRS intensity for MBZ-TP system was proportional to the concentration of MBZ in certain ranges. Fig. 2B shows the linear relationship of MBZ concentration with RRS intensities. So, the RRS method could be applied to the determination of MBZ.

FDS spectra

The FDS spectra of MBZ, TP and their ion–association complex are shown in Fig. 3. From Fig. 3A, it could be seen that under the experimental conditions, the FDS intensities of MBZ and TP alone were very weak; when the MBZ reacted with TP to form ion–association complex, the intensities of FDS were enhanced greatly. When $\lambda_{em}/\lambda_{ex}$ was 392/784 nm (FDS), the intensities of FDS reached their highest value. Fig. 3B shows that the enhancement intensity of FDS was directly proportional to the concentration of MBZ. Therefore FDS method could be applied to determine MBZ.

Absorption spectra

The absorption spectra of MBZ, TP and the complex are shown in Fig. 4. Fig. 4A shows that the maximum absorption wavelength of TP is located at 260 nm and that MBZ has weak absorption in had very weak absorption in 220–350 nm range. But the absorbance intensity of TP is enhanced after the reaction of TP with MBZ to form an ion–association complex. Fig. 4B demonstrates that there is a linear relationship between MBZ concentrations with the absorbance in a certain range, so that the content of MBZ can be determined by spectrophotometry.