

## Determination of thiabendazole in aqueous solutions using a cucurbituril-enhanced fluorescence method

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**Abstract** The complexation of thiabendazole (TBZ) with the cucurbit[6]uril (Q[6]), cucurbit[7]uril (Q[7]) and symmetric tetramethyl-cucurbit[6]uril (TMeQ[6]) in aqueous solution has been investigated using UV–vis and fluorescence spectrometry. The experimental results show 1:1 host–guest inclusion complexes at pH 6.5 for all three macrocyclic hosts, and the corresponding formation constants by UV and fluorescence methods are  $(5.37 \pm 1.05) \times 10^4 \text{ L mol}^{-1}$  and  $(1.47 \pm 0.41) \times 10^4 \text{ L mol}^{-1}$  for the Q[6]-TBZ system  $(7.76 \pm 0.51) \times 10^4 \text{ L mol}^{-1}$  and  $(9.36 \pm 0.22) \times 10^4 \text{ L mol}^{-1}$  for the Q[7]-TBZ system  $(1.28 \pm 0.78) \times 10^4 \text{ L mol}^{-1}$  and  $(2.69 \pm 0.55) \times 10^4 \text{ L mol}^{-1}$  for the TMeQ[6]-TBZ system, respectively. Based on the enhancement of the fluorescence intensity of TBZ with the addition of Q[n]s in neutral media, a fluorescence spectrometry method for the determination of TBZ in aqueous solution in the presence of Q[n] was established. In the range of  $6.0 \times 10^{-8} \text{ mol L}^{-1}$ – $8.0 \times 10^{-6} \text{ mol L}^{-1}$

a linear relationship was obtained between fluorescence intensity and TBZ concentration. The detection limit was found to be between 5.51 and  $8.85 \times 10^{-9} \text{ mol L}^{-1}$ . The interference of coexisting ions was found to be slight. The proposed method has been successfully applied to the determination of TBZ in different aqueous solutions with satisfactory recoveries of 92–103%. The method seems to be suitable for environmental water analysis.

**Keywords** Cucurbituril · Thiabendazole · Fluorescence spectroscopy · Supramolecular complex

### Introduction

One of the main sources of contamination in rivers and other water reserves is the unlimited and inadequate use of pesticides for controlling a wide variety of biological contaminants. This practice causes adverse effects on the human health and the environment and is a critical problem worldwide. As a consequence, new legislation in developed countries has established ppm or ppb ranges to reflect the maximum residue limit (MRL) for allowable pesticides [1].

Benzimidazole fungicides are systemic pesticides widely used in agriculture for protection against and eradication of a variety of pathogens which affect fruits and vegetables. Thiabendazole (TBZ) (Fig. 1) is an example of a benzimidazole compound. In view of its wide application, considerable work has been carried out on its detection and quantification. Various methods such as high-performance liquid chromatography (HPLC) [2], liquid chromatography-mass spectrometry (LC-MS) [3], solid phase extraction high-performance liquid chromatography (SPE-HPLC) [4], solid phase micro-extraction high-performance liquid chromatography-fluorescence (SPME-HPLC-fluorescence)

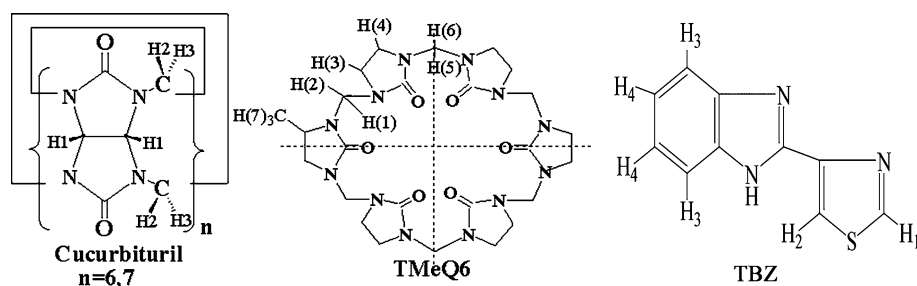
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**Fig. 1** Structures of cucurbiturils and thiabendazole



[5], ion-exchange chromatography-fluorescence (IEC-fluorescence) [6] have been employed to determine TBZ in a variety of matrices such as fruit, vegetables and fruit juice. Most of these methods were carried out in an organic medium, and required time-consuming and laborious pre-processing steps such as liquid extraction, solid phase extraction and supercritical fluid extraction. Fluorescence spectroscopy has been applied to quantitative analysis due to its inherent sensitivity. The development of methods that enhance the signals from fluorescent compounds allows for their analytical determination in very low amounts. Therefore, the development of a novel, highly sensitive and selective fluorescence spectroscopy method for the direct determination of TBZ in aqueous solution has important application value.

Cyclodextrins (CDs), the cyclic oligosaccharides consisting of six or more D-(+)-glucopyranose units are well known to have a hollow truncated cone with a hydrophobic cavity and a hydrophilic wall to form inclusion complexes with guest organic or inorganic molecules that possess suitable polarity and dimension. New methods with high sensitivity and selectivity for the determination of drugs and pesticides in aqueous solution have been established on the basis of the significant enhancement in the absorbance or fluorescence intensity of drug molecules produced through complexation with CDs [7–12]. Cucurbit[n]urils with a hydrophobic cavity and two opening dipole portals [13–16] can interact with different organic molecules to form various inclusion or exclusion host–guest complexes [17–20]. The formation of these complexes can modify the physicochemical properties of the guests, such as increasing their fluorescent intensity, and the method was applied to detect guest molecular [21–24]. In particular, Q[n] has an effect on the photophysical and photochemical properties of fluorescent dyes. e.g., solubilization, deaggregation, suppression of surface adsorption, fluorescence enhancement, increase in brightness, prolongation of fluorescence lifetimes, photostabilization, and increase the pKa values of included dyes [25]. As a result, new methods for the determination of guests have been established on the basis of the enhancement in the fluorescence intensity of guests molecules produced through complexation with Q[n]. For example, a novel sensitive Q[n] fluorescent sensor for the

detection of melamine [26], coptisine [27], sanguinarine [28] and  $\gamma$ -Hydroxybutyric acid [29] are reported. Moreover, the benzimidazole fungicides [30–32] have also been studied for Q[n] inclusion. Saleh and Pozo reported the 1:1 or 1:2 complex formation between carbendazim and Q[6, 7] and provided a sensitive and selective analytical procedure for determination of carbendazim. Saleh demonstrated that larger pKa shifts can be achieved with Q[7] when thiabendazole was selected as guest.

In the present paper, we describe the detailed study of the interactions between TBZ and Cucurbiturils (Q[6], Q[7] and TMeQ[6]) (Fig. 1). Cucurbiturils has been investigated as a fluorescent sensitizer for the determination of TBZ. A comparison with other HPLC methods has also been undertaken. The method applied to the determination of TBZ in different sources gives good recoveries.

## Experimental

### Materials

Thiabendazole (TBZ) (Sigma–Aldrich, Inc., St. Louis, USA) was obtained from Sigma and used without further purification. Cucurbit[n]urils (Q[6], Q[7] and TMeQ[6]) were prepared and purified according to the published methods [16, 33]. All other reagents were of analytical grade and were used as received.

### UV–vis spectra and fluorescence measurement

UV absorption spectra of the host–guest complexes were recorded on an Agilent 8453 Photospectrometer (Hewlett Packard, California, USA) at room temperature. Fluorescence spectra of the host–guest complexes were recorded on a Varian photofluorescent spectrometer (Varian Inc., California, USA) at room temperature. The aqueous solutions of thiabendazole were prepared at a concentration of  $1.00 \times 10^{-3} \text{ mol L}^{-1}$ . Aqueous solutions of Q[6] ( $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ), Q[7] ( $2.0 \times 10^{-4} \text{ mol L}^{-1}$ ) and (TMeQ[6]) ( $2.0 \times 10^{-4} \text{ mol L}^{-1}$ ) were prepared for both absorption spectra and fluorescence spectra determination. Samples of these solutions were combined to give solutions

with a Q[n]:TBZ ratio of 0, 0.2:1, 0.4:1, 1:1, ...4:1, respectively. The pH of the solution was  $\sim 6.5$ .

For fluorescence spectra the photomultiplier gain was medium with 5 nm emission and excitation bandwidths. The maxima excitation and emission wavelengths ( $\lambda_{EX}/\lambda_{EM}$ ) were 296 nm/357 nm for TBZ (pH = 6.5). The addition of Q[6], Q[7] and TMeQ[6] produced blue shifts of 6 nm in the maxima excitation. Therefore, the maxima excitation and emission wavelengths ( $\lambda_{EX}/\lambda_{EM}$ ) were 302 nm/355 nm, 302 nm/358 nm and 302 nm/355 nm at pH = 6.5 for the Q[6]-TBZ, Q[7]-TBZ and TMeQ[6]-TBZ systems, respectively. The fluorescence quantum yields were determined by the corrected spectra method and were calculated by the comparative method relative to quinine sulfate ( $a = 0.55$ ) [34, 35]. All the determinations were carried out at  $25.0 \pm 0.1$  °C.

#### Analytical parameters for TBZ

To obtain the calibration data, solutions of TBZ in the  $6 \times 10^{-8}$ – $8 \times 10^{-6}$  mol L<sup>-1</sup> concentration range were prepared by adding the corresponding aliquot of the stock concentrated solution in the presence and absence of the receptors Q[6], Q[7] or TMeQ[6] ( $4 \times 10^{-5}$  mol L<sup>-1</sup>) at pH = 6.5 and 25 °C. In accordance with IUPAC, the blank solution was measured ( $n \geq 20$ ) for the determination of standard deviation ( $S_B$ ), the precision and the detection limit ( $LOD$ ) of the method.

#### Recovery in water

Solutions of TBZ (30–80  $\mu$ M) containing 10% (v/v) water and Q[n] (Q[6], Q[7] and TMeQ[6] (40  $\mu$ M) were prepared by adding an aliquot of the concentrated solution of the guest and the host and diluting with buffer solution pH = 6.5. TBZ residues were not detected in blank solutions.

#### Water sample analysis

Water samples were filtered through a 0.45  $\mu$ m membrane filter (Science Reagent Co., Ltd. Guiyang, China) and collected in glass bottles pre-cleaned with hydrochloric acid, and were then stored in a 4 °C refrigerator (Haier Group, Qingdao, China).

The samples of TBZ (30–80  $\mu$ M) were prepared by adding a suitable volume of the concentrated solution of pesticide, the corresponding Q[n] concentration (40  $\mu$ M) and the required volume of water to a 10 mL volumetric flask. This was diluted with buffer solution pH = 6.5. The concentration of water in the final solutions to be analysed was 10% (v/v). The method of standard addition (MOSA)

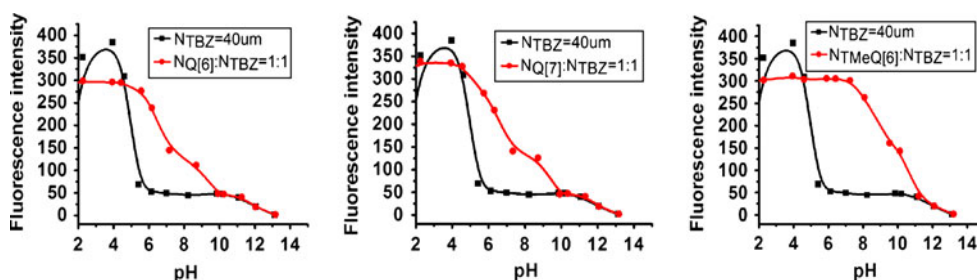
was used for the apparent recoveries (definition recommended by IUPAC [36] for triplicate analysis).

## Results and discussion

Thiabendazole presents three pKa values ( $pK_{a1} = -0.5$ ,  $pK_{a2} = 4.8$  and  $pK_{a3} = 11.3$ ), it is protonated on the imidazole ring in acid solutions ( $pK_{a2} = 4.8$ ), and protonation of the thienyl ring to form a dication does occur at a very low pH ( $pK_{a1} = -0.5$ ). Thus, it exists as a cation protonated on the imidazole ring at pH values below 5, as a neutral molecule in the pH range 5–11, and as an anion at pH values greater than 11 [37]. The energy fluorescence transition of thiabendazole are only slightly affected by pH ( $\lambda_{max} = 351$  nm in 2.4 N HCl,  $\lambda_{max} = 349$  nm in 0.01 N HCl and  $\lambda_{max} = 353$  nm in buffer pH 7.6). However, the fluorescence intensity is strongly pH dependent. In strong acid and alkaline solutions, the compound has a low fluorescence intensity, while in a weak acidic solution, the fluorescence intensity shift to very high signal. In the present study, the influence of solution pH on Q[n]-TBZ complexation was investigated by using fluorescence spectroscopy at different pH values (in the range of 2–12). Figure 2 shows fluorescence intensity at  $\lambda_{ifmax}$  versus pH for TBZ (40  $\mu$ M) and TBZ-Q[n] (Q[6], Q[7] and TMeQ[6]) (40  $\mu$ M:40  $\mu$ M). One can see an obvious fluorescence intensity difference between free TBZ and the bound TBZ at  $pH \geq pK_{a2}$ , and pKa values shift up to 5 units, when the protonated form is the major species in solution. These results are in good agreement with the reference describing the preference of Q[7] for binding positively charged guests [38]. This suggests that the selected Q[n]s interact with the protonated pesticide through the ion–dipole interaction.

#### Fluorescence properties

The absorption ( $\lambda_a$ ) and fluorescence ( $\lambda_{em}$ ) wavelength maxima of the compound were measured as a function of media. The absorption wavelength maxima were found to be insensitive to solvent; however, the fluorescence transition energies, given in Table 1 and Fig. 3, generally shift to blue wavelengths with the cucurbit[n]urils. Thiabendazole have fluorescence quantum yield of  $\sim 0.045$ ,  $\sim 0.067$  and  $\sim 0.057$  in water, methanol and ethanol at room temperature, respectively. Upon addition of Q[n], the quantum yield of TBZ increased by two to threefold, probably because of the thiabendazole encapsulated inside cucurbiturils.

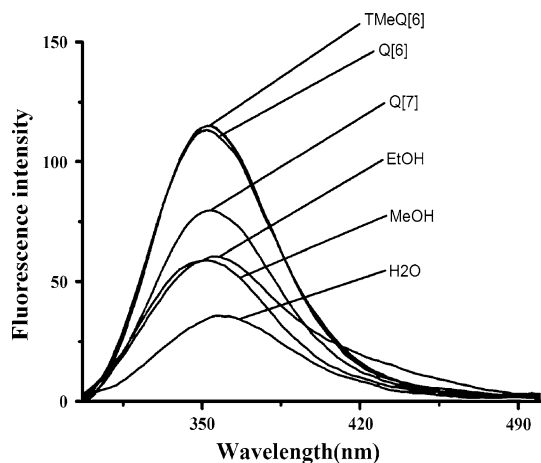


**Fig. 2**  $I_{fmax}$  versus pH curves of TBZ recorded in the absence and in the presence of 1.0 equiv. of Q[n]

**Table 1** Photophysical parameters of TBZ in different media under air<sup>a</sup>

Medium	Wavelength maxima (nm)		Quantum yield ( $\Phi_f$ )
	$\lambda_a$	$\lambda_{em}$	
Water	298	358	0.045
MeOH	299	354	0.067
EtOH	300	352	0.057
Q[6]	302	352	0.12
Q[7]	301	354	0.089
TMeQ[6]	302	354	0.13

<sup>a</sup> From ref. [34, 35]



**Fig. 3** Fluorescence emission spectra of TBZ in different media under air

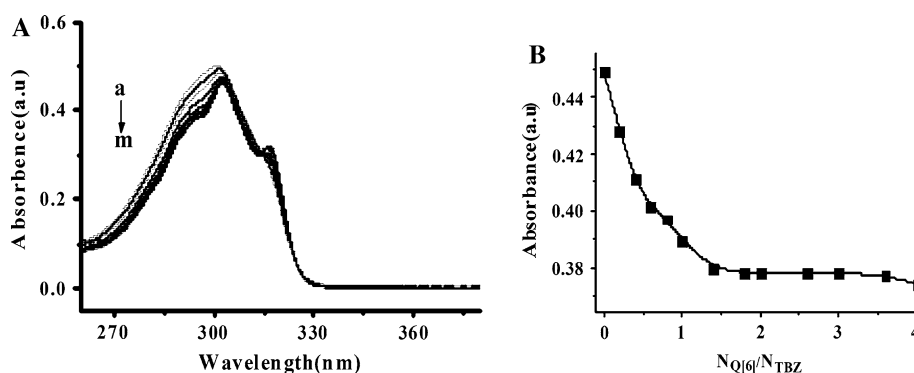
### UV–vis and fluorescence behaviour in cucurbiturils

The UV spectra obtained with aqueous solutions containing a fixed concentration of the guest (40  $\mu$ M) and variable concentration of Q[6] are shown in Fig. 4. As can be seen, the absorption spectra of TBZ exhibited a common progressively lower absorbance with a slight red shift as the ratio of  $N_{Q[6]}/N_{TBZ}$  was increased and a new peak appeared at 316 nm wavelength (Fig. 4a). The host shows no absorbance in the range of  $>210$  nm. The absorbance

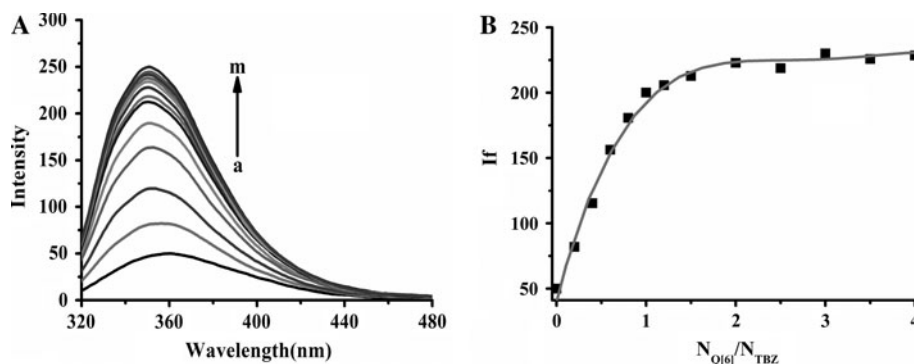
(A) versus ratio curves can be fitted to a 1:1 binding model for the Q[6]-TBZ system (Fig. 4b) and the Q[7]-TBZ and TMeQ[6]-TBZ systems can be seen to have similar UV absorption spectra (referring to supporting information, Fig. 1S and Fig. 2S). The corresponding formation constants ( $K$ ) are:  $(5.37 \pm 1.05) \times 10^4$  L mol<sup>-1</sup> for the Q[6]-TBZ system  $(7.76 \pm 0.51) \times 10^4$  L mol<sup>-1</sup> for the Q[7]-TBZ system and  $(1.28 \pm 0.78) \times 10^4$  L mol<sup>-1</sup> for the TMeQ[6]-TBZ system [38].

Fluorescence emission spectra and the corresponding  $I_f$  versus  $N_{Q[6]}/N_{TBZ}$  curve of 40  $\mu$ M TBZ in the presence of increasing concentrations of Q[6] at  $\lambda_{EX}/\lambda_{Em} = 302/355$  nm are shown in Fig. 5. In contrast with the UV absorption spectra, the fluorescence spectra of TBZ exhibited progressively higher intensity with the shift in blue wavelength upon addition of increasing amounts of Q[6] to the solution. The effect of fluorescence enhancement of TBZ in cucurbituril solution may be due to the formation of a host–guest inclusion complex, which protects the TBZ fluorescent singlet state thus increasing the fluorescence quantum yield of the guest. The fluorescence intensity ( $I_f$ ) versus ratio curves can be best fitted to a 1:1 binding model for the Q[6]-TBZ system, which was consistent with those obtained from the absorption spectrophotometric analysis. For Q[7]-TBZ and TMeQ[6]-TBZ systems, it can be seen to have similar fluorescence spectra (referring to supporting information, Fig. 3S and Fig. 4S). The corresponding formation constants ( $K$ ) are:  $(1.47 \pm 0.41) \times 10^4$  L mol<sup>-1</sup> for the Q[6]-TBZ system  $(9.36 \pm 0.22) \times 10^4$  L mol<sup>-1</sup> for the Q[7]-TBZ system  $(2.69 \pm 0.55) \times 10^4$  L mol<sup>-1</sup> for the TMeQ[6]-TBZ system respectively. They are quite close to those obtained by absorption spectrophotometric analysis (as shown in Table 2).

The results show that there is an interaction between TBZ and Q[6], Q[7] and TMeQ[6] which produced significant enhancement of the fluorescence intensity of TBZ as a result of the complexation with Q[n]. On the basis of the above work, a spectrophotometric method with improved sensitivity for the determination of TBZ in aqueous solution was developed.



**Fig. 4** UV absorption spectrum of TBZ in the presence of increasing concentrations of Q[6] ( $a \rightarrow m = 0 \rightarrow 1.6 \times 10^{-4} \text{ mol L}^{-1}$ ) (a) and corresponding absorbance versus  $N_{Q[6]}/N_{TBZ}$  curves at  $\lambda_{\text{max}} = 300 \text{ nm}$  (b)



**Fig. 5** Fluorescence emission spectra (a) and corresponding  $I_f \cdot N_{Q[6]}/N_{TBZ}$  curves (b) ( $a \rightarrow m = 0 \rightarrow 1.6 \times 10^{-4} \text{ mol L}^{-1}$ ) for the Q[6]-TBZ system

**Table 2** Formation constant (K) of Q[n] with TBZ

Host-guest systems	$K_{UV} (\text{L mol}^{-1})$	$K_{IF} (\text{L mol}^{-1})$
Q[6]-TBZ	$(5.37 \pm 1.05) \times 10^4$	$(1.47 \pm 0.41) \times 10^4$
Q[7]-TBZ	$(7.76 \pm 0.51) \times 10^4$	$(9.36 \pm 0.22) \times 10^4$
TMeQ[6]-TBZ	$(1.28 \pm 0.78) \times 10^4$	$(2.69 \pm 0.55) \times 10^4$

**Analytical parameters**

To evaluate the analytical potential of the Q[n] approach, we have created calibration graphs for a range of TBZ concentrations,  $6.0 \times 10^{-8} - 8.0 \times 10^{-6} \text{ mol L}^{-1}$  at  $\text{pH} = 6.5$  in the presence of  $40 \mu\text{M}$  Q[6], Q[7] and TMeQ[6] respectively, at  $25 \text{ }^\circ\text{C}$  and the analytical parameters were calculated according to the IUPAC definition ( $3.29s_B/m$ ). All data are given in Table 3 together with the standard

deviation of the blank signal ( $s_B$ ), calibration sensitivity ( $m$ ), limits of detection ( $LOD$ ) and relative standard deviations ( $RSD$ ). The calibration graphs obtained by plotting relative fluorescence intensity versus concentration were linear (at least 10 different concentrations) and had good correlation coefficients (at least 0.9998). In the presence of Q[6] and TMeQ[6] the value of  $m$  (slope of the calibration graph) was the same, and slightly higher than that in Q[7] in water solutions, and the value  $s_B$  (standard deviation of the blank of at least 11 replicates) showed the same trend as the value of  $m$ . The  $LODs$  were particularly low, ranging from  $5.51$  to  $8.85 \times 10^{-9} \text{ mol L}^{-1}$ . The precision of the method was determined by analysing 10 replicate samples of  $1.6 \times 10^{-6} \text{ mol L}^{-1}$  of TBZ and the relative error was found to be not higher than 5%. The detection limit of this method is comparable with that of other methods described in the analytical literature as shown in Table 4. The

**Table 3** Analytical parameters

Species	$s_B$	$M (\times 10^6 \text{ L mol}^{-1})$	$LOD (\times 10^{-9} \text{ mol L}^{-1})$	$RSD (\%)$
Q[6]-TBZ	0.31	$130.45 \pm 0.13$	$7.13 \pm 0.02$	1.41
Q[7]-TBZ	0.21	$114.27 \pm 0.24$	$5.51 \pm 0.01$	1.34
TMeQ[6]-TBZ	0.39	$132.25 \pm 0.30$	$8.85 \pm 0.02$	0.87



**Table 4** Methods for determination of TBZ in different matrices

Samples	Detection technique	LOD (ng mL <sup>-1</sup> )
Water	Fluorescence [39]	26.2
Water	Solid phase fluorimetry [40]	0.1
Water	HPLC [41]	1.0
Water	This method	1.1

**Table 5** Effects of foreign species on the determination of  $1 \times 10^{-6}$  mol L<sup>-1</sup> thiabendazole

Ions or species	Foreign species/TBZ (mol L <sup>-1</sup> /mol L <sup>-1</sup> ) <sup>a</sup>
K <sup>+</sup> , Cl <sup>-</sup> , Na <sup>+</sup>	450
Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup>	130
SiO <sub>3</sub> <sup>2-</sup>	220
Fe <sup>3+</sup> , Al <sup>3+</sup>	50
Spermine, Spermidine	50
Histamine	5

<sup>a</sup> Maximum tested tolerance level

detection limit of this method is the same as that of the HPLC method mentioned in the literature. However, this method is direct and simple and requires only the addition of Q[7] at neutral pH and room temperature. In addition it is not time consuming and no organic solvents are required. Thus thiabendazole was detected directly using

cucurbit[n]urils as a fluorescence—sensitizing agent, and it is expected to be more widely used in different pesticides.

#### Effect of the presence of other species

Cucurbit[n]urils are the compounds with a hydrophobic cavity and two opening dipole portals, they are able to form stable complexes with biogenic amines, such as diamines [42], amines [43], dialkyl- and diarylammonium ions [44] with affinity of  $10^2$ – $10^9$  M<sup>-1</sup>. Furthermore, cucurbit[n]urils can coordinate with metal ions, such as the alkali and alkaline earth cations [45–47] and form Q[n]-based complexes. The stability constants between guests and the Q[n]s will be affected in the presence of cations as a result of cation capping of the portals of the Q[n]s.

A study was carried out on the effects of foreign species on the determination of  $1.60 \times 10^{-6}$  mol L<sup>-1</sup> of TBZ. A certain concentration of ions and biogenic amines which interfere with TBZ was tested first, in the case of interference, the ratio was reduced gradually until the interference ceased. The criterion for interference was fixed at a  $\pm 5\%$  variation of the average fluorescence intensity calculated for an established level of TBZ. The results are shown in Table 5, and as can be seen the concentration of these ions and biogenic amines is greater than normally allowed for the particular TBZ content, there also appears to be little interference between multiple ions, thus indicating that the presence of these ions and biogenic amines

**Table 6** Study of TBZ recovery in samples of waters

Sample	Added (10 <sup>-6</sup> mol L <sup>-1</sup> )	Found (10 <sup>-6</sup> mol L <sup>-1</sup> ) <sup>a</sup>	This method		HPLC	
			Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Tap water <sup>b</sup>	1.60	1.47	91.99	2.22	96.78	1.83
	3.20	3.01	94.17	1.43	98.96	1.12
Mineral water <sup>c</sup>	1.60	1.53	95.88	0.49	97.61	0.65
	3.20	3.22	100.62	0.65	99.40	0.34
Mineral water <sup>d</sup>	1.60	1.57	98.43	0.46	97.67	0.89
	3.20	3.32	103.61	0.75	101.32	0.87
Mineral water <sup>e</sup>	1.60	1.47	91.87	0.95	91.65	0.76
	3.20	3.06	95.69	1.33	96.34	0.69
River water <sup>f</sup>	1.60	1.53	95.32	0.89	96.73	1.23
	3.20	3.17	98.95	0.54	99.81	0.39

<sup>a</sup> This data are the average of three independent determinations

<sup>b</sup> From Guiyang City

<sup>c</sup> From Hebei province. This water contains Ca<sup>2+</sup>  $\geq$  400  $\mu$ g/100 mL, Mg<sup>2+</sup>  $\geq$  50  $\mu$ g/100 mL, K<sup>+</sup>  $\geq$  35  $\mu$ g/100 mL, Na<sup>+</sup>  $\geq$  80  $\mu$ g/100 mL, SiO<sub>3</sub><sup>2-</sup>  $\geq$  80  $\mu$ g/100 mL, pH 7.3  $\pm$  0.5

<sup>d</sup> From Chongqing city. This water contains K<sup>+</sup> (1.0–27.0 mg/L), Cl<sup>-</sup> (1.0–24.0 mg/L), Mg<sup>2+</sup> (0.1–5.0 mg/L), SO<sub>4</sub><sup>2-</sup> (0.4–20.0 mg/L)

<sup>e</sup> From Huangguoshu landscape of Guizhou province. This water contains Sr<sup>2+</sup>: 0.1–1 mg/L, SiO<sub>3</sub><sup>2-</sup>: 8.0–25.6 mg/L, Zn<sup>2+</sup>: 0.006–0.10 mg/L, Se<sup>2+</sup>: 0.0001–0.04 mg/L, K<sup>+</sup>: 0.1–0.8 mg/L, Na<sup>+</sup> 2–5 mg/L, Ca<sup>2+</sup>: 55–70 mg/L, Mg<sup>2+</sup>: 4.0–8.0 mg/L, Natural free CO<sub>2</sub>: 3–6 mg/L, HCO<sub>3</sub><sup>-</sup>: 100–150 mg/L, SO<sub>4</sub><sup>2-</sup>: 50–60 mg/L, Cl<sup>-</sup>: 3–7 mg/L

<sup>f</sup> From the Huaxi river

does not affect the detection of TBZ unless the ratio of foreign species/TBZ ( $\text{mol L}^{-1}/\text{mol L}^{-1}$ ) is larger than the value listed in the table. Therefore, it is clear that the proposed method has excellent selectivity.

#### Analytical applications

This method of TBZ determination was carried out in real samples of different aqueous solutions. The expected generic environmental concentration for TBZ in surface waters was found to be approximately  $2.5 \text{ ng ml}^{-1}$  [48]. Because the samples used did not contain pesticides at levels higher than the detection limits, a recovery study was carried out (Table 6) by spiking the samples with TBZ. At the same time, the amount of TBZ in the samples was also determined using HPLC as a reference method.

In this study, different types of waters, tap water, several different brands of mineral water and river water from Huixi(China) were analysed after the appropriate additions of TBZ; the results are shown in Table 6. The experimental results showed that the recovery rates were in the range 92–103% which is very similar to that obtained using the HPLC method.

#### Conclusion

In conclusion, this work provides a method for testing pesticide residues in water. The proposed method is a simple, fast and cheap alternative to other methods since it avoids the use of toxic organic solvents and laborious pre-processing steps such as liquid extraction, solid phase extraction and supercritical fluid extraction etc. The method showed good recoveries according to current guidelines. Further studies involving the application of the proposed method to other matrices are in progress.

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