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ORIGINAL PAPER

Microwave-assisted sensing of tetracycline using europium-sensitized luminescence fibers as probes

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Abstract In this paper, we describe a facile approach—using silicate fibers immobilized with Eu(III) ions [Eu(III) fibers] as affinity probes—to rapidly sense tetracycline (TC) in complex samples. The fabrication of the Eu(III) fibers is straightforward: Simply immerse a silicate fiber into a glass tube containing Eu(III) and irradiate with microwaves (power, 900 W) for 30 s. The Eu(III) fibers selectively trap TC from aqueous samples via chelation of the β-diketone functional group of TC with the Eu(III) center. Because the Eu(III)–TC complexes on the fibers are luminescent, as a result of intermolecular energy transfer from the TC moieties to the Eu(III) centers, they can be detected directly using a fluorophotometer. To accelerate the sensing process, we also used microwave irradiation (for only 15 s) to trap the TC molecules from the sample solutions onto the Eu(III) fibers. Furthermore, only a small volume (< 10 μL) of sample solution is required for these analyses. This approach allows TC to be detected in aqueous samples, with a detection limit of 50 nM.

Keywords Europium · Tetracycline · Luminescence · Microwave heating

Introduction

Solid phase microextraction (SPME) under microwave heating is used to accelerate the extraction of target species from complex samples [1–9]. Once the target species are attached to the SPME fiber, they can be readily detected using suitable detection methods. Most SPME methods, however, require the target species to be eluted from the SPME fiber prior to detection. If the fibers bearing the target species could be analyzed directly, then the elution steps would be unnecessary and sample loss could be avoided. Laser desorption/ionization mass spectrometric analysis of target species-bound SPME fibers has been demonstrated previously [10, 11]. Although elution is not required prior to introducing the fibers into the mass spectrometer, the instrument is expensive. Therefore, the development of less expensive analytical tools for direct detection of fiber-bound target species remains a considerable challenge. Colorimetric and luminescence detection methods are commonly employed in chemical sensing [12–17].

Tetracycline (TC) is a broadband antibiotic for both Gram-positive and Gram-negative bacterial strains. It is used widely as feed additive to promote the growth of livestock. Its extensive use may result in TC residues remaining in meat-based foodstuffs. Many analytical methods have been developed for the analysis of TC [18–31]. Among them, exploiting the intermolecular energy transfer from TC to Eu(III) ions is a particularly useful means of detecting TC selectively through suitable analytical detection methods [23–28]. Hirschy et al. [23] developed a straightforward method to quantify TC in aqueous samples via the detection of the red luminescence from intermolecular energy transfer from TC to Eu(III) ions. One problem associated with such approaches, however, is that water molecules can strongly quench the luminescence from excited trivalent europium ions because the energy gap between the luminescence state and the ground state is ca. 12,000 cm^{-1} for Eu(III), which is close to the third vibration overtone of proximate OH

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oscillators (ν_{OH}=ca. 3,300–3,500 cm^{-1}) [32, 33]. The addition of surfactants [24–28] or ethylenediaminetetra-acetic acid [33] is an effective means of stabilizing and enhancing the Eu(III)-sensitized luminescence of TC in aqueous solutions.

Our aim in this study was to develop a straightforward method for directly sensing analytes on SPME fibers. As an alternative method of reducing the quenching effects of water molecules in aqueous solutions, we investigated the use of silicate fibers immobilized with Eu(III) ions as probes to selectively trap TC from aqueous samples. Because microwave-assisted heating can be used to accelerate the mass transfer of the target species onto their adsorbents, we bound Eu(III) ions onto the surface of silicate fibers via electrostatic interactions under the assistance of microwave irradiation. We then used the fibers immobilized with Eu(III) ions [Eu(III) fibers] to selectively trap TC from aqueous solutions via β-diketone chelation—again, under microwave irradiation for a short period of time. Introducing the target species-bound fibers directly into a fluorophotometer allowed us to detect the luminescence emitted from the Eu(III)–TC complexes. That is, the Eu(III) ions on the Eu(III) fibers are used as both the adsorbent and the luminescence reporter for TC.

To achieve the goal for rapid screening purpose, the newly developed method should have the detection limit lower than the maximum residue limit for tetracycline, oxytetracycline, and chlortetracycline set by European Union (EU) Regulation No. 2377/90, Food and Agriculture Organization, and World Health Organization (according to the data provided in http://www.inchem.org/documents/jecfa/jeceval/jec_2243.htm). The maximum residue limits for milk and eggs are 0.1 mg/L and 0.4 mg/kg, respectively. Thus, we aimed to develop a rapid screening method, which can provide a low detection limit.

Experimental

Reagents and materials Europium(III) acetate hydrate was purchased from Acros (Belgium, NJ, USA). Nitric acid (HNO_3, 65%) and chlortetracycline hydrochloride (from *Streptomyces aureofaciens*) were obtained from Fluka (Buchs, Switzerland). Hydrochloric acid (35%), hydrofluoric acid (HF, 48%), and trifluoroacetic acid (99.5%) were obtained from Merck (Seelze, Germany). Phosphoric acid (85%) was obtained from Riedel–de Haën (Seelze, Germany). Ethanol, ampicillin (AC), tris(hydroxymethyl) aminomethane (Tris), oxytetracycline dihydrate, and TC were purchased from Sigma (St. Louis, MO, USA). Acetone and methanol were obtained from Tedia (Fairfield, OH, USA). Optical fibers (125 μm o.d.) were kindly provided as a gift from Hua Eng Wire and Cable Co., Ltd (Kaohsiung, Taiwan). Millex®GS filters (pore size, 0.22 μm) were purchased from Millipore (Ireland). Open glass tubes (1.1 mm o.d.) were purchased from a local company (Dung-Kun, Hsinchu). Concentrated chicken soup powder was purchased from a grocery store. Human serum samples were obtained from Hsinchu Mackay Memorial Hospital (Hsinchu, Taiwan), donated by healthy individuals.

Fabrication of Eu(III)-immobilized fibers An optical fiber (18 mm long, 125 μm o.d.) was immersed in acetone for 15 min, and then its polymer shell was removed using a pair of tweezers. The fiber was rinsed twice with methanol and deionized water and then sonicated in deionized water for 3 min to remove any impurities. The fiber was dried using a hair dryer. A glass tube (15 mm long, 1.1 mm o.d.) was placed into a solution containing Eu(III) ions (10 mM). The solution filled the glass tube via capillary action. The volume of the solution in the tube was estimated to be 9.25 μL, based on weighing the tube before and after filling with the solution and assuming that the density of the solution was 1 g/cm^3. Next, the fiber was inserted to the glass tube filled with the Eu(III) solution, followed by incubation in a microwave oven (power, 900 W) for 30 s. The amount of Eu(III) bound to the fiber was determined from the luminescence of Eu(III)–TC complexes on the fiber after using various microwave powers and incubation times. That is, the Eu(III) fibers obtained above were placed in a tube (10 mm long) containing a TC solution (6.22 μL), and then it was subjected to luminescence detection. Furthermore, the amount of Eu(III) bound to the fiber was estimated using inductively coupled plasma mass spectrometry (ICP-MS). The ions were eluted from the fiber by immersing it for 2 h in a solution containing HNO_3 (65%, 0.5 mL) and HF (48%, 0.1 mL). The solution was then diluted to 10 mL with deionized water and subjected to ICP-MS analysis.

Microwave-assisted sensing of TC by Eu(III)-immobilized fibers Prior to performing sensing experiments, a TC stock solution (0.01 M) was prepared afresh by dissolving these antibiotics in ethanol, while oxytetracycline and chlortetracycline stock solutiona (0.01 M) were prepared in methanol. Samples were then prepared by diluting the stock solutions to expected concentrations with Tris buffer (25 mM, pH 7.5). Chicken soup was prepared by dissolving concentrated soup powder (0.4 g) in Tris buffer (25 mM, pH 7.5, 40 mL) that was stirred and heated in a water bath maintained at 100 °C. After cooling to room temperature, a given amount of TC was spiked into the soup. The soup was centrifuged at 6,000 rpm, filtered through a Millipore filter, and then centrifuged at 12,000 rpm. Serum samples were prepared by diluting serum (0.4 mL) with Tris buffer

(25 mM, pH 7.5, 9.6 mL). A given concentration of TC was spiked into the serum samples.

To begin the trapping experiments, an open glass tube (1.1 mm o.d., 10 mm long) was placed into sample solutions containing various concentrations of TC. The TC solution filled the tube via capillary action. The density of the solution was assumed to be 1 g/cm^3. Thus, the volume of the solution in the tube was estimated to be 6.22 μL, based on the weight of the tube before and after its filling with the solution. A Eu(III) fiber obtained as described above was placed into the glass tube containing the TC sample and incubated in a microwave oven (power, 270 W) for 15 s. After rinsing by deionized water, the fiber was dried using a hair dryer and then placed diagonally in a microvolume cell for fluorescence spectroscopic analysis (bandpass, 5 nm; see Fig. 1). The light path was estimated ca. 146 μm. The excitation wavelength was set at 397.5 nm. The maximum luminescence wavelength was ca. 616 nm. The intensity at 616 nm was used to obtain calibration curves and plots by subtracting the intensity of the baseline, which was obtained from the average of the intensities at 606 and 626 nm in each spectrum.

Instrumentation Fluorescence spectra were obtained using a Horiba Jobin Yvon FluoroMax®-3 spectrophotometer (NJ, USA). ICP-MS results were obtained using a Sciex Elan 5000 apparatus (Perkin–Elmer, USA).

Results and discussion

To obtain our analytical probes sensing probes for TC, our first step was preparing the Eu(III)-immobilized fibers by binding Eu(III) ions onto the surfaces of silicate fibers through electrostatic interactions. We employed microwave irradiation to heat the samples and accelerate the binding of the Eu(III) ions onto the fibers. The content of immobilized Eu(III) ions on the fiber was investigated in terms of the luminescence resulting from the fiber-bound Eu(III)–TC complexes after treatment with a TC solution. Figure 2a displays the luminescence obtained after binding Eu(III) ions onto fibers under microwave power of 900 W for 30 s and at room temperature (ca. 25 °C) for 10 h, followed by interacting with sufficient amounts of TC under microwave heating at 270 W for 15 s. The luminescence intensities at 616 nm of the Eu(III)–TC complexes on the fibers obtained using these two approaches were comparable. That is, similar amounts of Eu(III) ions were bound to the fibers in each case. We also employed ICP-MS—after eluting the Eu(III) ions from the Eu(III) fibers—to determine the contents of immobilized Eu (III) ions; we found that there were ca. 35.4 pmol of Eu(III) ions immobilized on each fiber. Figure 2b displays the luminescence obtained after using our Eu(III) fibers to trap TC from aqueous samples under microwave irradiation at 270 W for 15 s and at room temperature (ca. 25 °C) for 15 s. The luminescence intensity was much higher when we performed the trapping experiment under microwave irradiation than it was at room temperature. That is, microwave-induced heating did indeed accelerate the binding of TC onto the surfaces of the Eu(III) fibers.

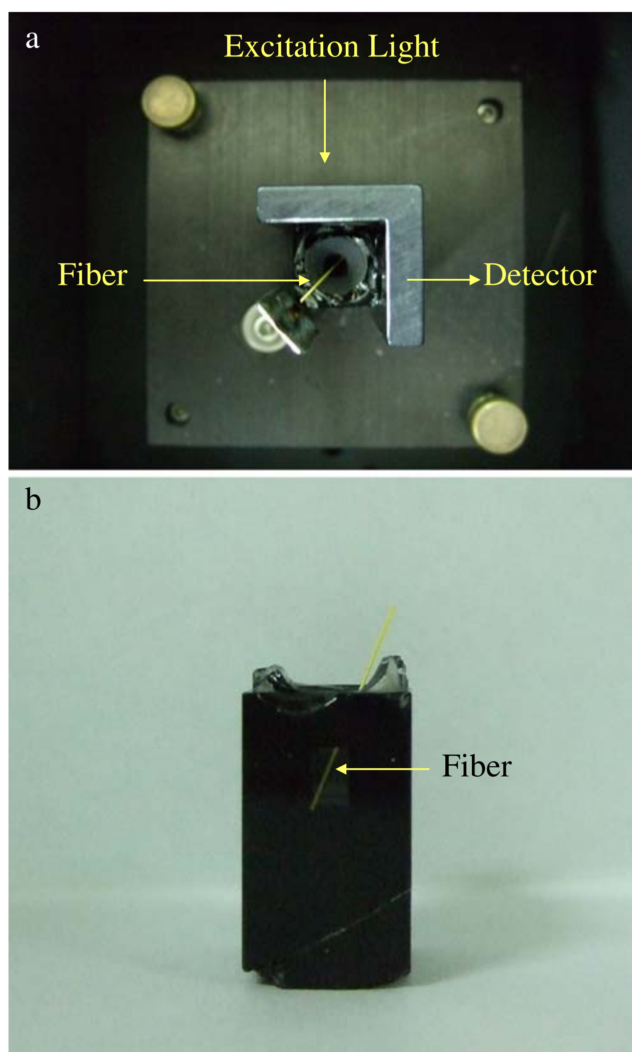


Fig. 1 **a** The position of a fiber in a detection cell and **b** the cross profile of the cell. The fiber was placed diagonally in a microvolume cell. For ease of visibility, the yellow polymer shell of the fiber was not removed

To determine the optimal pH for the binding of TC onto the Eu(III) fibers, we measured the luminescence (Fig. 3) of Eu(III) fibers that we had treated with TC samples prepared in Tris buffers having various values of pH. The binding of TC with Eu(III) at pH 7.5 provided the highest luminescence intensity at a wavelength of 616 nm. Thus, in our subsequent experiments, the sample solutions were all adjusted to pH 7.5 prior to trapping.

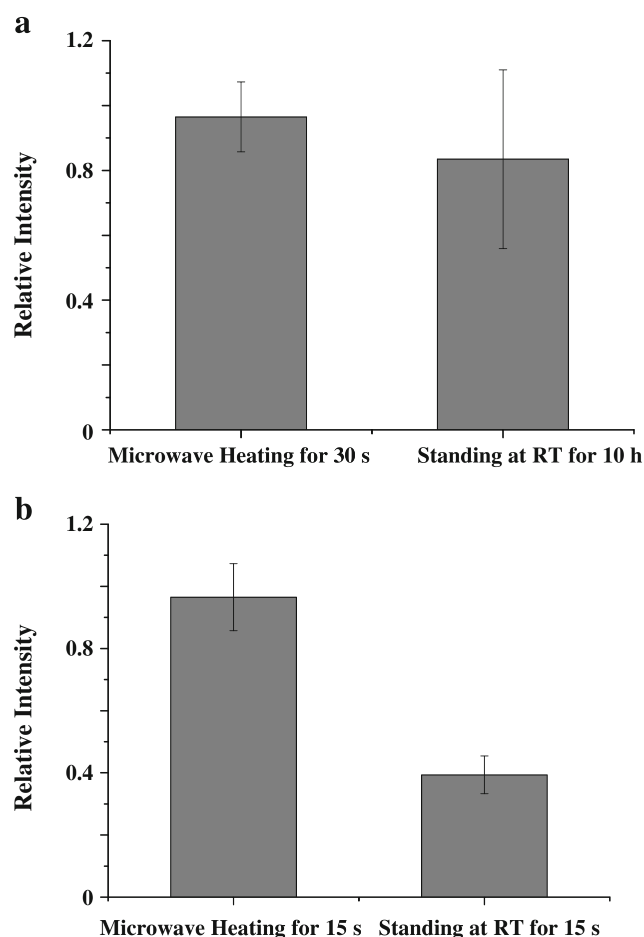


Fig. 2 Luminescence intensities ($\lambda_{emission}$=616 nm) obtained after **a** binding Eu(III) ions to the fiber under microwave irradiation (power, 900 W) for 30 s (*left bar*) and at room temperature (ca. 25 °C) for 10 h (*right bar*), followed by interaction with TC under microwave irradiation at 270 W for 15 s and luminescence detection, and **b** using the Eu(III) fibers to selectively trap TC from aqueous samples under microwave irradiation at 270 W for 15 s (*left bar*) and at room temperature (ca. 25 °C) for 15 s (*right bar*), followed by luminescence detection. The fibers were placed directly into a fluorophotometer for detection ($\lambda_{excitation}$=397.5 nm). The relative intensity was obtained based on the ratio of the intensity at peak maximum (I_M) subtracting its base line intensity at $\lambda_{616\ nm}$ (I_B) to I_B, *i.e.* [(I_M)-(I_B)]/[I_B]. The baseline intensity (I_B) was determined by averaging the intensity at $\lambda_{616\ nm}$ and $\lambda_{626\ nm}$ in each spectrum

Figure 4a presents the emission intensities at 616 nm obtained after using the Eu(III) fibers to trap target species from TC samples of various concentrations, followed by luminescence detection. The luminescence intensity increased linearly upon increasing the concentration of TC in the sample solution. The detection limit is estimated ca. 50 nM based on the result. Figure 4b presents the corresponding luminescence spectra. The maximum fluorescence appeared at a wavelength of ca. 616 nm when the excitation wavelength was 397.5 nm. The emission band that appeared at ca. 595 nm derived presumably from the Raman scattering of the fiber because this band also appeared in the spectrum of an unmodified fiber. Furthermore, this band shifted upon changing the excitation wavelength. To estimate the amount of TC bound to each Eu(III) fiber, we measured the change in fluorescence intensity of the TC solution before (10^{-4} M) and after its interaction with the Eu(III) fibers. The result suggested that ca. 62.2 pmol of TC was trapped by each fiber, i.e., each Eu (III) ion on the fiber was capable of chelating ca. 2.64 TC molecules. Previous studies have determined that TC units form between seven and nine coordinate bonds to Eu(III) ions in aqueous solution [34–36]. Therefore, because TC is a bidentate ligand, between two and four TC molecules should bind to each Eu(III) ion. Scheme 1 presents our proposal for the binding structure of TC on each Eu(III) fiber.

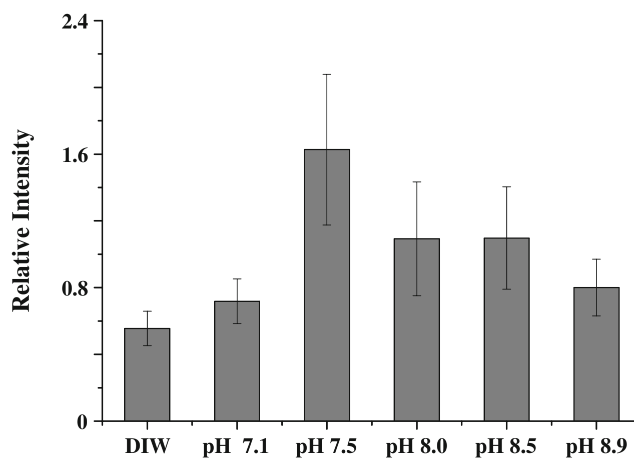


Fig. 3 Luminescence intensities ($\lambda_{emission}$=616 nm) obtained after using Eu(III) fibers to trap target species from TC samples prepared in Tris buffers of various pH, followed by luminescence detection. The fibers were placed directly into a fluorophotometer for detection ($\lambda_{excitation}$=397.5 nm). The relative intensity was obtained based on the ratio of the intensity at peak maximum (I_M) subtracting its base line intensity at $\lambda_{616\ nm}$ (I_B) to I_B, *i.e.* [(I_M)-(I_B)]/[I_B]. The baseline intensity (I_B) was determined by averaging the intensity at $\lambda_{616\ nm}$ and $\lambda_{626\ nm}$ in each spectrum. *DIW* deionized water (pH ~ 6.5)

To examine the selectivity of the Eu(III) fibers toward TC, we investigated the competitive binding of a solution containing TC and another common antibiotic, AC (inset to Fig. 5), which does not possess a β-diketone functional group. Figure 5 reveals that the luminescence intensities at 616 nm were similar after using the Eu(III) fibers as probes to trap the target species from the TC and TC/AC solutions. The presence of AC in the sample only slightly affected the binding of TC on the Eu(III) fiber.

TC-derived compounds with similar tetracycline-plane modified with different functional groups, including oxytetracycline and chlortetracycline, have been widely used as antibiotics. To investigate if this current approach is suitable for the analysis of TCs as a group, we initially examined whether oxytetracycline and chlortetracycline individually can be analyzed by this approach. Figure 6a,

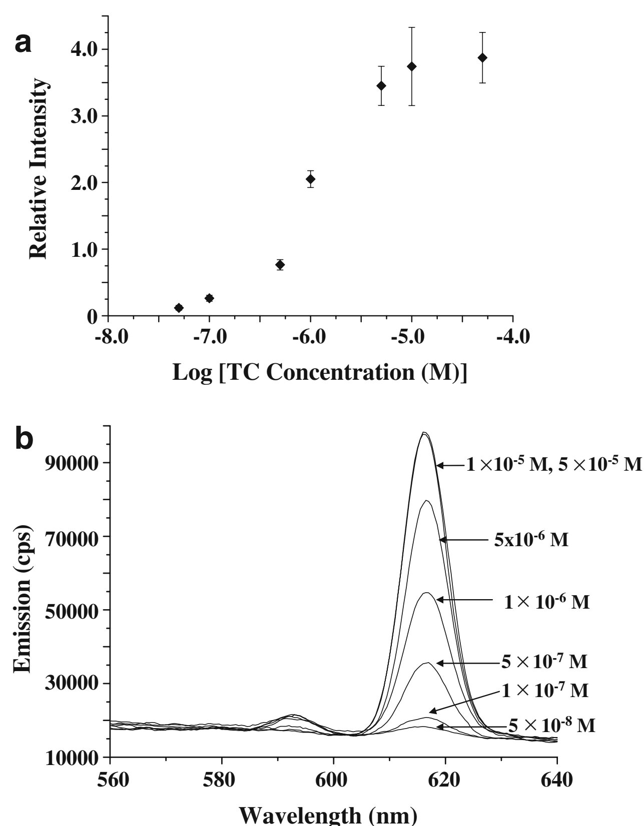
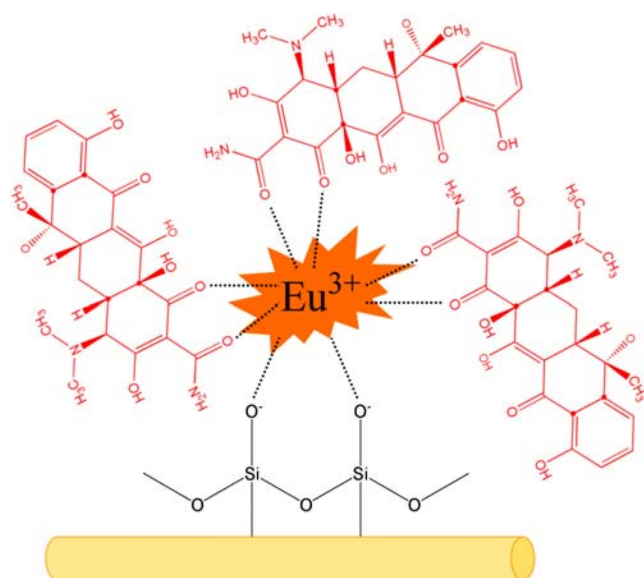


Fig. 4 **a** Luminescence intensity at 616 nm of Eu(III) fibers after trapping TC from aqueous samples plotted with respect to the concentration of TC. **b** Corresponding luminescence spectra. The fibers were placed directly into a fluorophotometer for detection ($\lambda_{excitation}$=397.5 nm). The relative intensity was obtained based on the ratio of the intensity at peak maximum (I_M) subtracting its base line intensity at $\lambda_{616\ nm}$ (I_B) to I_B, *i.e.* [(I_M)-(I_B)]/[I_B]. The baseline intensity (I_B) was determined by averaging the intensity at $\lambda_{616\ nm}$ and $\lambda_{626\ nm}$ in each spectrum



Scheme 1 Proposed structure of TC units interacting with a Eu(III) ion on the surface of a Eu(III) fiber

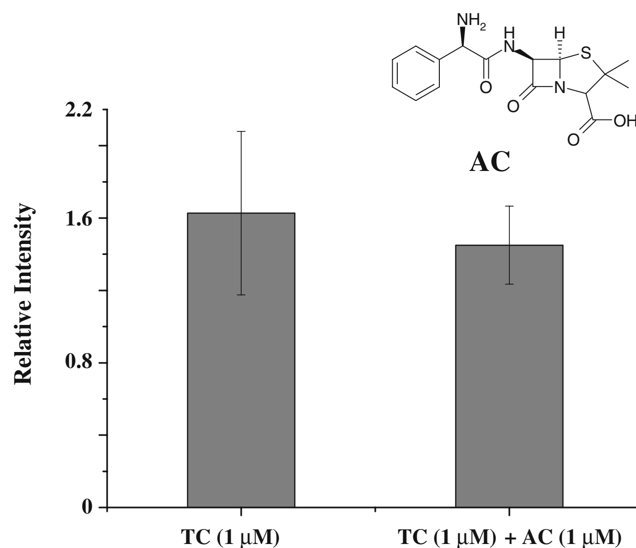


Fig. 5 Luminescence intensities ($\lambda_{emission}$=616 nm) obtained after using the Eu(III) fibers to trap target species from a mixture of TC (1 μM) and AC (1 μM) and from TC (1 μM) alone (*right bar*), followed by luminescence detection. The fibers were placed directly into a fluorophotometer for detection ($\lambda_{excitation}$=397.5 nm). The relative intensity was obtained based on the ratio of the intensity at peak maximum (I_M) subtracting its base line intensity at $\lambda_{616\ nm}$ (I_B) to I_B, *i.e.* [(I_M)-(I_B)]/[I_B]. The baseline intensity (I_B) was determined by averaging the intensity at $\lambda_{616\ nm}$ and $\lambda_{626\ nm}$ in each spectrum

b presents the emission intensities at 616 nm obtained after using the Eu(III) fibers to trap target species from oxytetracycline and chlortetracycline samples, respectively, of various concentrations, followed by luminescence detection. The luminescence intensity increased linearly upon increasing the concentration of the antibiotics in the sample solution, and the luminescent intensity is saturated around the concentration of 10^{-5}M. The saturated intensity is lower than that using TC as the samples (cf. Fig. 4a). The results demonstrated that the approach is also suitable for the analysis of TC-derived antibiotics although the resultant luminescence is weaker than that obtained from a TC sample at the same concentration. It might be contributed from the differences of the functional groups attached on these TCs. We further used a TC mixture, including TC, oxytetracycline, and chlortetracycline, with equal concentrations as the sample for examination. Figure 6c presents the emission intensities at 616 nm obtained after using the Eu(III) fibers to trap target species from the sample of various concentrations, followed by luminescence detection. The result is similar to that obtained in Fig. 6a, b. That is, the luminescence intensity increased linearly upon increasing the concentration of the antibiotics in the sample solution, and the luminescent intensity is saturated around the concentration of 10^{-5} M as well. The detection limit is ca. 10^{-7} M, i.e. ca. 0.04 mg/L, which is lower than the maximum residue limit (0.10 mg/L) in milk regulated by

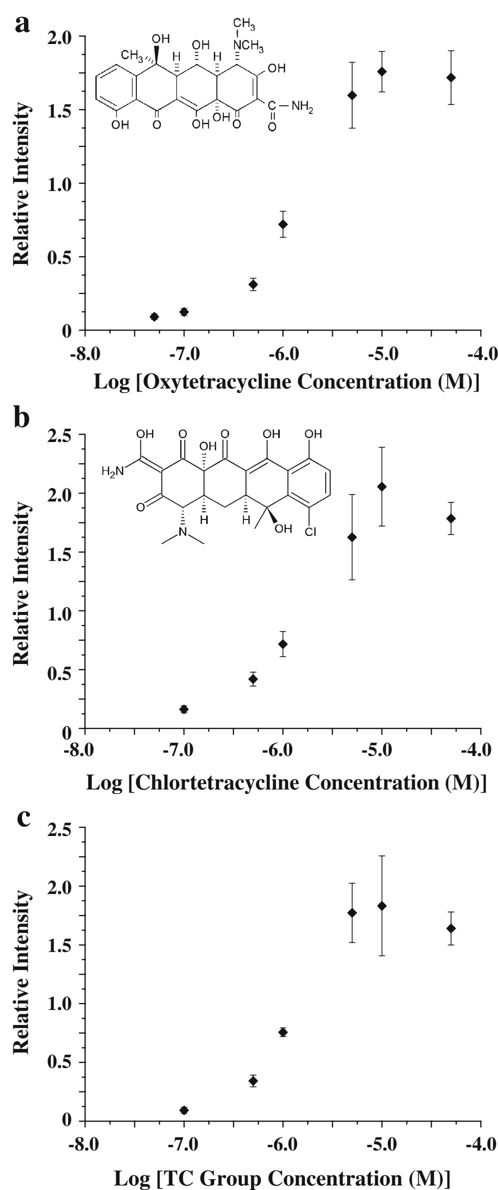


Fig. 6 **a** Luminescence intensity at 616 nm of Eu(III) fibers after trapping oxytetracycline, **b** chlortetracycline, and **c** the mixture containing equal concentration of TC, oxytetracycline, and chlortetracycline from aqueous samples prepared in Tris buffer (25 mM, pH 7.5) plotted with respect to the total concentration of the antibiotics

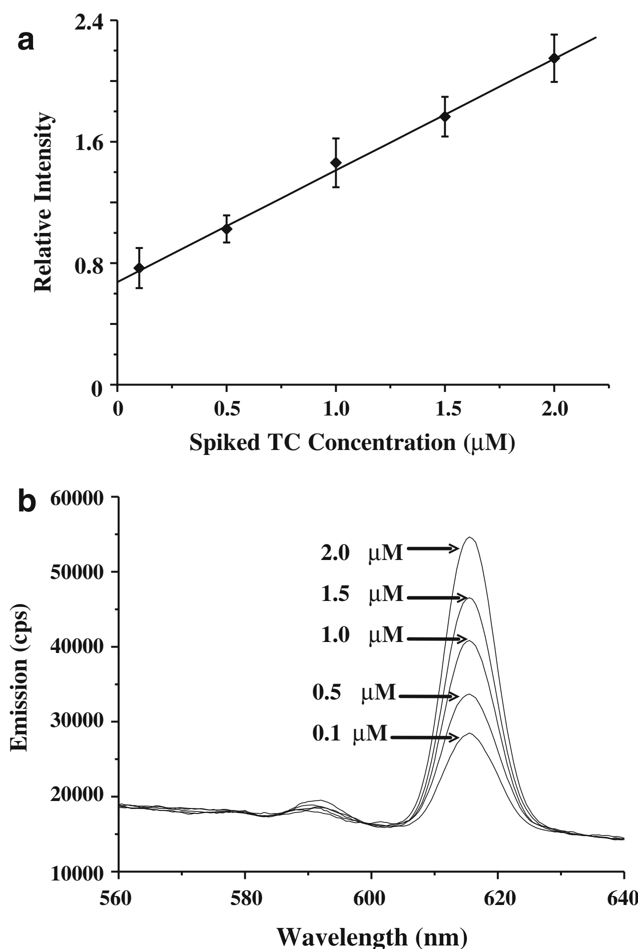


Fig. 7 **a** Calibration curve, obtained using the standard addition method, displaying the relative luminescence intensity at 616 nm of Eu(III) fibers after trapping TC from chicken soup samples (followed by direct luminescence detection) plotted with respect to the concentration of TC. **b** Corresponding luminescence spectra. The fibers were placed directly into a fluorophotometer for detection ($\lambda_{excitation}$=397.5 nm). The relative intensity was obtained based on the ratio of the intensity at peak maximum (I_M) subtracting its base line intensity at $\lambda_{616\ nm}$ (I_B) to I_B, *i.e.* [(I_M)-(I_B)]/[I_B]. The baseline intensity (I_B) was determined by averaging the intensity at $\lambda_{616\ nm}$ and $\lambda_{626\ nm}$ in each spectrum

the EU. The result demonstrates that this approach is applicable to the analysis of the TC group samples.

To demonstrate the applicability of using this approach in a real-world application, we employed a chicken soup sample spiked with TC (10^{-6} M) as the analytical sample. Because the complex matrix in the soup sample affected the luminescence of the TC–Eu(III) complexes, we reduced the matrix effect by employing a standard addition method for quantitative analysis. Figure 7a displays the calibration curve (Y=0.67005X+0.72237; R^2=0.9980) obtained after plotting the luminescence intensity at 616 nm obtained after using the Eu(III) fiber as a probe with respect to the concentration of TC in the chicken soup samples; Fig. 7b presents the corresponding luminescence spectra. Using this calibration curve, we estimated the concentration of TC in our analytical sample to be 1.078×10^{-6} M. Although this value deviates by ca. +7.8% from the true value (1.0×10^{-6} M), this result demonstrates that it is possible to estimate the concentrations of TC in complex samples using this approach.

Next, we examined the feasibility of using this approach to determine the concentration of TC in a serum sample that was spiked with TC (1.0×10^{-6} M). Again, we used the standard addition method for quantitative analysis. The resulting calibration curve (Y=0.33522X+0.37304; R^2=0.981). Our estimated value for the concentration of TC in the spiked

serum sample was 1.113×10^{-6}M, i.e., a deviation of 11.3% from the true value. We suspect that this deviation resulted from the extremely small sample volume, the very short analysis time, and errors arising from personal handling of the sample. The detection limit of TC in such complex samples was ca. 8×10^{-7} M based on a signal-to-noise ratio of 3.

Conclusions

We have developed a straightforward method for the rapid screening of TC from complex samples, in which the luminescence of Eu(III)–TC complexes on silicate fibers is measured after introducing the sensing probes directly into a fluorophotometer. Using this approach, there is no need to perform any tedious sample pretreatment or elution steps prior to detection. Because we used microwave irradiation to accelerate the binding of TC to the Eu(III) fibers, the time required for the entire analysis was extremely short; indeed, it was possible for us to complete the entire analysis within 5 min. The detection limit of TC in aqueous samples is also lower then that set by EU regulations. Additionally, when employing the probe to sense TC from complex samples, we obtained concentrations that deviated by ~10% from the true values. Because of its simplicity, speed, low sample consumption, and low cost, we believe that, after further improvement, this sensing method has potential for use in the rapid screening of TC in various complex samples.

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