Ratio Fluorescence Detection of Tetracycline by Eu$^{3+}$/NH$_2$-MIL-53(Al) composite

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Table 1 Comparison of This Method with Reported Tetracycline Sensors.

| Methods       | Materials                        | Linear range | LOD       | Ref |
|---------------|----------------------------------|--------------|-----------|-----|
| LC-MS/MS      | -                                | 25-200 µg/kg | 2.22-3.59 µg/kg | 1   |
| CE            | -                                | 25-250 µg/L  | 2-9 µg/L  | 2   |
| Fluorometry   | FeOx@SiO<sub>2</sub> -FMIPs      | 0.2-6 µM     | 117 nM    | 3   |
| Fluorometry   | CDs                              | 2-150 µM     | 520 nM    | 4   |
| Fluorometry   | Eu-EDTA+surfactant               | 0.2-5 µM     | 0.2 µM    | 5   |
| Fluorometry   | NH<sub>2</sub>-MIL-53(Al)        | 1.5-70 µM    | 0.92 µM   | This work |
| Fluorometry   | Eu<sup>3+</sup>/NH<sub>2</sub>-MIL-53(Al) | 0.5-60 µM | 0.16 µM   | This work |
Fig. S1 The fluorescence reversibility of the probe in aqueous solution
Fig. S2 The linear relationship between the TC concentration of different concentrations in the actual water sample and the ratio of the fluorescence intensity of the probe.

Table 2 The Results for the Determination of TC in Real Samples.

| Sample     | Added (μM) | Founded (μM) | Recovery (n=3,%) | RSD (n=3,%) |
|------------|------------|--------------|------------------|-------------|
| Tap water  | 20         | 20.6526      | 103.26           | 5.9966      |
|            | 30         | 30.4321      | 101.44           | 1.5346      |
|            | 40         | 38.0127      | 95.03            | 2.4287      |
Fig. S3  Selectivity of fluorescent probes to aureomycin, terramycin, tetracycline, demeclocycline at room temperature
[1] S. O. S. Mookantsa, S. Dube, M. M. Nindi, Development and application of a dispersive liquid-liquid microextraction method for the determination of tetracyclines in beef by liquid chromatography mass spectrometry. Talanta 148 (2016) 321-328.
[2] Rodriguez Ávila, José Antonio. Magnetic solid phase extraction based on phenyl silica adsorbent for the determination of tetracyclines in milk samples by capillary electrophoresis. J. Chromatogr. A 1218 (2011) 2196-2202.
[3] J. Ashley, X. T. Feng, Y. A Sun, multifunctional molecularly imprinted polymer-based biosensor for direct detection of doxycycline in food samples. Talanta 182 (2018) 49-54.
[4] M. Lin, H. Y. Zou, T. Yang, et al. An inner filter effect based sensor of tetracycline hydrochloride as developed by loading photoluminescent carbon nanodots in the electrospun nanofibers. Nanoscale 8 (2016) 2999-3007.
[5] J. Zhang, B. Zhang, Y. Wu, et al. Fast determination of the tetracyclines in milk samples by the aptamer biosensor. Analyst 135(10) (2010) 2706-2710.