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2 **Reusable DNA-Functionalized-Graphene for Ultrasensitive**
3 **Mercury (II) Detection and Removal**

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Abstract

Mercury is a bioaccumulative and highly toxic heavy metal. Thus, the removal and detection of Hg^{2+} from the environment is a major challenge. This paper reports a novel bio-nanomaterial for the simultaneous determination and removal of Hg^{2+} with the use of rGO- Fe_3O_4 functionalized with Hg^{2+} -specific thymine oligonucleotide (T-DNA). T-DNA interacts with Hg^{2+} and changes from having a random coil into a hairpin structure, thereby increasing the fluorescence of SYBR Green I. Such fluorescence turn-on process allows the detection of Hg^{2+} in the concentration range of 1 ng/mL to 20 ng/mL, with a detection limit of 0.82 ng/mL. Removal is achieved by exploiting the T- Hg^{2+} -T base pairs and the large surface area of graphene; these bio-nanocomposites exhibit excellent removal efficiency (over 80%) and rapid separation from the aqueous solution. Moreover, bio-nanomaterials can be regenerated after a simple treatment. The proposed method also demonstrates the evident practicability of the simultaneous detection and removal of Hg^{2+} in lake water samples.

Keywords: graphene, mercury, removal, detection, aptamers

1. Introduction

Heavy metal pollution is an important environmental concern that poses serious threats to human health. Mercury (II) ion is a well-known neurotoxin, and its accumulation, even at low concentrations, has led to severe health problems, including blindness, deafness, coordination loss, and death (Clarkson et al., 2003; Dorea et al., 2006; Nolan et al., 2008; Tchounwou et al., 2003). The contamination of drinking water and other natural water resources is a serious problem, as they are non-biodegradable resources that can enter into the food chain. Thus, an effective way should developed for the selective monitoring and effective removal of mercury contamination in water or wastewater generated by both natural processes and human activities.

Researchers have proposed several analytical protocols for routine analysis of Hg^{2+} , such as atomic absorption spectrophotometer (AAS)/atomic emission spectrometry (AES) (Ghaedi et al., 2006), auger-electron spectroscopy (Lu et al., 2012), and ICP-MS (Jia et al., 2011). However, mercury removal rely on traditional techniques such as ion exchange (Oehmen et al., 2006), mechanical filtration (Biester et al., 2000), chemical precipitation (Huttenloch et al., 2003), reverse osmosis, flotation (Chojnacki et al., 2004; Evangelista et al., 2007), membrane separation (Lopes et al., 2007), and selective liquid–liquid extraction (de Mendonça Fábrega et al., 2007). The majority of existing methods for Hg^{2+} detection and removal have been conducted separately, and an efficient means of utilizing these materials and technologies for the simultaneous determination and removal of mercury ion is yet to be proposed (Dave

et al., 2010; He et al., 2013).

An advanced material system with (1) a high sensitivity and (2) a high surface area with a high absorption coefficient is required to integrate the detection and absorption of Hg^{2+} . Originally, DNA-functionalized biosensors were reorganized as effective devices for detecting Hg^{2+} (Dave et al., 2010; Helwa et al., 2012). In the past decade, numerous studies have focused on developing materials for biosensor immobilization, such as silica, hydrogels (Liu et al., 2011; Nayak et al., 2005), carbon nanotubes (Zhu et al., 2010; Yang et al., 2008), graphene oxide (Lu et al., 2009; Loh et al., 2010; Huang et al., 2011; Liao et al., 2014), magnetic beads (Zhu et al., 2013), and polymers (Li et al., Lee et al., 2009). Most of these materials support chemical functional groups. Graphene oxide consists of a hexagonal network of carbon atoms that bear hydroxyl and epoxy functional groups and are mostly decorated by carboxyl groups (Huang et al., 2011; Qu et al., 2010; Kuilla et al., 2010; Wang et al., 2013). Given its remarkable properties, such as huge surface area and good chemical stability, graphene oxide is a good adsorbent for removing pollutants. However, graphene oxide is not extensively applied as an adsorbent, because it is difficult to separate from aqueous solutions that cause serious health and environmental problems. Therefore, the use of reduced graphene oxide (rGO), which can be achieved by combining graphene oxide with Fe_3O_4 and decorating it with magnetic nanoparticles (rGO- Fe_3O_4), is an effective approach to overcome separation problems (Sun et al., 2011). In recent years, several fluorescent, colorimetric, and electrochemical Hg^{2+} detection methods (Zhao et al., 2006; Lee et al., 2007; Huang et al., 2008) based on

the identification of Hg^{2+} -mediated base pairs (T- Hg^{2+} -T) have been developed (Miyake et al., 2006; Ono et al., 2004; Wang et al., 2008). The attachment of thymine-rich DNA to the backbone of rGO- Fe_3O_4 facilitates the simultaneous detection and removal of Hg^{2+} from water.

This paper reports thymine-rich DNA-functionalized graphene oxide based magnetic nanoparticles that allow the sensitive and selective detection of Hg^{2+} via fluorescence changes. Given that the DNA has been immobilized within the rGO- Fe_3O_4 , Hg^{2+} can be adsorbed by the DNA and the rGO- Fe_3O_4 , and can therefore be easily separated from the aqueous solution with the aid of the magnetic field. The sensitivity, selectivity, and reusability of this approach were demonstrated for ultrasensitive mercury removal and detection. The proposed method was successfully applied to determine and remove Hg^{2+} from spiked water samples.

2. Experimental

2.1. Materials. All DNA samples were purchased from Sangon Biotech (Shanghai, China) and purified using high-performance liquid chromatography. N, N-Dicyclohexyl carbodiimide (DCC), Amino-Hg-DNA (Amino-5'-CTTCTTTCTTCCCCCTTGTTTGTG), 1-Pyrenebutylacid, and N-hydroxysuccinimide were obtained from Aladdin (Shanghai, China). Graphite powder was purchased from Alfa Aesar. The 10000 $\times$ SYBR Green I in dimethyl sulfoxide (DMSO) was purchased from Invitrogen (Carlsbad, CA). AgNO_3 and other metal salts were of analytical reagent grade and purchased from Chengdu Kelong Chemical Reagent Co., Ltd. The supporting electrolyte was a 0.01 M phosphate buffer solution (PBS) prepared with Na_2HPO_4 and KH_2PO_4 , and the pH was adjusted with

NaOH or H₃PO₄. All reagents and solvents used in the synthesis were commercially available and utilized as received without any purification unless otherwise mentioned. All reagents, unless specified, were acquired from Beijing Chemical Agents. Deionized water (18.2 MΩ/cm) was used to prepare the solutions.

2.2. Synthesis of DNA/PASE-rGO-Fe₃O₄. The preparation of Fe₃O₄ and rGO-Fe₃O₄ is described in the Supplementary Materials. 1-pyrenebutanoic acid succinimidyl ester (PASE) was synthesized using the method mentioned by a previous study (Wu et al., 2008). A solution of N,N'-dicyclohexyl carbodiimide (DCC, 2.0 mmol) in dry tetrahydrofuran (THF, 10 mL) was added drop-wise to the stirred reaction mixture of 1-pyrenebutyl acid (2.0 mmol) and N-hydroxysuccinimide (2.0 mmol) in THF (50 mL) at 0 °C. After being stirred overnight at room temperature, the resulting mixture was filtered. The solvent was removed under reduced pressure to render the compound PASE as a yellow solid, which was purified through recrystallization from ethanol.

PASE-rGO-Fe₃O₄ was prepared according to the literature (Yang et al., 2008). A 2mg/mL PASE solution in dimethyl formamide (DMF) was mixed with 10 mg rGO-Fe₃O₄ for 2 h while stirring. The mixture was subsequently centrifuged at 12,000 rpm for 10 min to remove the supernatant. The resulting PASE-rGO-Fe₃O₄ composite was then dispersed in a 0.9 mL PBS (0.01 M pH 7.4) solution.

A 0.1 mL of 260 μmol/L Amino-Hg-DNA solution was mixed with a 0.9 mL PASE-rGO-Fe₃O₄ solution (see Fig. 1c). The mixture was kept at 4 °C for 24 h with occasional shaking. The solution was centrifuged at least 20 min at 12000 rpm and then washed repeatedly to remove the excess DNA. The other unreacted active groups

were blocked by adding amine-PEG-amine. This stock was stored under refrigeration (4 °C) before use. The final DNA concentration within rGO-Fe₃O₄ was determined using UV absorption (see Fig. S3).

2.2. Hg²⁺ Detection. An appropriate concentration of Hg²⁺ (within the range of 1 ng/mL to 100 ng/mL) was added to the PBS buffer (0.01mol/L, pH 7.4), followed by the addition of DNA-rGO-Fe₃O₄ (50 nM DNA) and 2×SYBR Green I to the solution, which was then carefully mixed. The mixture was incubated at room temperature for 30 min before the fluorescence was measured. Fluorescence intensity was recorded at 528 nm with a 485 nm excitation wavelength.

2.3. Adsorption experiments. A typical adsorption experiment was conducted by first adding 5 mg of the as-prepared DNA-rGO-Fe₃O₄ to 10 mL of the PBS buffer mixed solution (0.01mol/L, pH 7.4) containing 5 µg/mL of mercury ions, which was stirred for 170 minutes afterward. Then, the DNA-rGO-Fe₃O₄ with adsorbed mercury ions was separated from the mixture with permanent hand-held magnets. Lastly, supernatants were collected and acidified with 2% HNO₃ before the metal ion concentrations were determined by ICP-MS. Solutions with varying initial concentrations were treated with the abovementioned procedure at room temperature to obtain the adsorption isotherms of the heavy metal ions. Blank samples (containing only deionized water and the corresponding rGO-Fe₃O₄) were prepared and monitored as control throughout the experiment.

Adsorption capacity (q_e , mg/g), which indicated the adsorption amount of heavy metal ions at equilibrium, was calculated according to the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where C_0 is the initial heavy metal ions concentration in the solution (mg/L), C_e is the equilibrium concentration (mg/L) after adsorption, V is the solution volume (L), and m is the mass of DNA-rGO-Fe₃O₄ adsorbent (g).

3. Results and discussion

3.1. Characterization. Fe₃O₄ magnetic nanoparticles (Fe₃O₄ MNPs), rGO-supported Fe₃O₄ MNPs (rGO-Fe₃O₄), and DNA- rGO-Fe₃O₄ were prepared using co-precipitation method (Yan et al., 2014; Paul et al., 2015). The scanning electronic microscopy (SEM) image of Fe₃O₄ MNPs shows a granular morphology (Fig. S1), and the rGO-Fe₃O₄ composite (Fig. 2a) displays a layered graphene structure. The observed granular particles of Fe₃O₄ MNPs indicates the growth of Fe₃O₄ MNPs along the graphene sheets. The transmission electron microscope (TEM) image of the rGO-Fe₃O₄ composite (Fig. S2) also shows folded graphene sheets coated with Fe₃O₄ MNPs, further confirming the growth of Fe₃O₄ MNPs along the graphene sheets. To confirm the chemical composition of the Fe₃O₄ MNPs and rGO-Fe₃O₄, the powders were characterized by X-ray diffraction (Fig. 2b). Diffraction peaks at 30.21°, 35.58°, 43.35°, 53.30°, 7.10°, and 62.57° were observed on the Fe₃O₄ MNPs and are attributed to the (220), (311), (400), (422), (511) and (440) planes of the Fe₃O₄ MNPs, respectively. The same set of characteristic peaks was observed for the rGO-Fe₃O₄, thus indicating the stability of the crystalline phase of Fe₃O₄ MNPs in the nanohybrid and confirming the attachment of NPs onto GO. A broad peak of

approximately 24° appears in the XRD patterns of rGO-Fe₃O₄ and stems from the rGO, which may be attributed to the lack of graphene sheet stacking (Ayyappan et al., 2011). The magnetization curves of Fe₃O₄ MNPs and rGO-Fe₃O₄ are presented in Fig. 2c. The values of saturation magnetization (Ms) are 37.7 and 54.6 emu g⁻¹, which are both lower than that of the corresponding bulk material (92 emu g⁻¹).

3.2. Hg²⁺ detection with DNA- rGO-Fe₃O₄. This study used a thymine-rich DNA (referred to as Amino-Hg-DNA) as attachment to the rGO-Fe₃O₄ through the PASE solution (Fig. 1b). A series of investigations were conducted. Figure 3a shows the fluorescence changes of SYBR Green I under different conditions. In the absence of Hg²⁺, the DNA adopts a random coil structure to which the addition of SYBR Green I results in a weak fluorescence (Fig. 3a, blue line). The SYBR Green I gives a weaker fluorescence in the presence of graphene oxide (Fig. 3a, red line) than in the solution without graphene oxide, given that graphene oxide causes fluorescence quenching due to fluorescence resonance energy transfer (FRET). In the presence of Hg²⁺, the DNA forms a hairpin structure to which SYBR Green I binds, thereby increasing the emission by twofold (Fig. 3a, pink line).

3.3. Hg²⁺ detection sensitivity and selectivity. A series of Hg²⁺ concentrations from 1 ng/mL to 100 ng/mL were investigated to evaluate the sensitivity of this fluorescence turn-on method. The fluorescence intensity gradually increased with increasing Hg²⁺ concentrations, as illustrated in Fig. 3b. The relative fluorescence intensity (F/F₀) initially increased linearly with [Hg²⁺] (Figs. 3c and d) and then saturated at 50 ng/mL Hg²⁺. The detection limit was determined at 0.82 ng/mL

(defined as $3\sigma/\text{slope}$, where σ was the relative standard deviation of a blank solution, such that $\sigma = 2.96\%$ and $\text{slope} = 0.109$), which was lower than the 10 nM mercury or 2 parts-per-billion reported by the U.S. Environmental Protection Agency. The comparison results of Hg^{2+} detection using different methods are shown in Table S1. F_0 and F refer to the fluorescence intensity of SGI-DNA- rGO- Fe_3O_4 (SGI referred to SYBR Green I) complex in the absence and presence of Hg^{2+} , respectively. Other environmentally relevant metal ions, such as Ag^+ , Zn^{2+} , Mg^{2+} , Al^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ca^{2+} , and K^+ were investigated under the same conditions as Hg^{2+} to examine the selectivity of the method. In this experiment, 500 ng/mL of the other metal ions and the 100 ng/mL of Hg^{2+} were added to the solution. The results are shown in Fig. 4. The highest fluorescence change was observed in the presence of Hg^{2+} , whereas minimal fluorescence change was noted with large amounts of other metal ions.

3.4. Adsorption kinetics. The effects of contact time on the adsorption capacities of the DNA-rGO- Fe_3O_4 and rGO- Fe_3O_4 were investigated within the time range of 0 to 190 min (Fig. 5a). DNA loading accelerated the adsorption process, and 170 min were needed for the DNA-rGO- Fe_3O_4 and rGO- Fe_3O_4 to reach the adsorption equilibrium for Hg^{2+} . Interestingly, similar Hg^{2+} removal kinetics was also observed (black line) for the prepared rGO- Fe_3O_4 without the DNA. This finding can be explained by the ability of graphene oxide to adsorb Hg^{2+} because of its large surface area and its functional groups on the surface (Guo et al., 2014; Warner et al., 2009). All kinetic data are used for fitting the pseudo-first-order and pseudo-second-order equations expressed as follows:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t and q_e are the amounts of Hg^{2+} adsorbed at time t and at equilibrium, respectively (mg/g). The k_1 (min) and k_2 (g/mg·min) are the equilibrium rate constant of the pseudo-first-order and pseudo-second-order equations, respectively.

The fitting plots using pseudo-first-order and pseudo-second-order equations are shown in Figs. 5b and 5c. The kinetic parameters acquired from the fitting results are summarized in Table S2.

The linear plot of t/q versus t (Fig. 5b, red line for DNA-rGO- Fe_3O_4 and black line for rGO- Fe_3O_4 , respectively) displays a good agreement between the experimental and calculated q_e values. The R^2 values for the second-order kinetic model are over 0.99 (Table S2), which confirms the applicability of this equation and the second-order nature of the adsorption process on DNA-rGO- Fe_3O_4 and rGO- Fe_3O_4 .

3.5. Isotherm modeling. The equilibrium behavior of metal uptake was fitted into the Henry, Langmuir, and Freundlich equations sorption isotherm model to obtain basic knowledge of DNA-rGO- Fe_3O_4 and rGO- Fe_3O_4 as a sorbent. The models are expressed as follows:

Henry model:

$$q_e = kC_e \quad (4)$$

Langmuir model:

$$q_e = \frac{bq_m C_e}{1 + bC_e} \quad \frac{1}{q_e} = \frac{1}{bq_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

Freundlich model:

$$q_e = k_F C_e^{1/n} \quad \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (6)$$

where q_e is the adsorption amount of Hg^{2+} on adsorbent (mg/g) at an equilibrium state (Pyrzynska et al., 2010; Moradi et al., 2010; Vuković et al., 2010), q_m is the adsorption capacity of metals on adsorbent (mg/g), and C_e is the equilibrium concentration of Hg^{2+} ions (ng/mL). Furthermore, k is the Henry constant related to the affinity of binding sites, b is the Langmuir adsorption constant, related to the adsorption energy, and k_F (adsorption capacity of adsorbent) and n (favorability of adsorption process) are the Freundlich constants.

All isotherms displayed a similar shape and were nonlinear over a wide range of aqueous equilibrium concentrations in Figs. 5d–5f. The results of the adsorption isotherm obtained through linear regression procedures are shown in Table S3. Figure 5d shows the Henry adsorption isotherm for Hg^{2+} on DNA-rGO- Fe_3O_4 (red line) and rGO- Fe_3O_4 (black line). The correlation coefficients (R^2) of the linear plot are 0.980 and 0.986. For the Langmuir adsorption isotherm model, the linear plot of $1/q_e$ vs. $1/C_e$ suggests that both adsorbents conform to the Langmuir isotherm model, with correlation coefficients (R^2) higher than 0.99 (Fig. 5e). The q_m values, calculated from the slope of each calibration graph, were found to be 180.18 and 124.84 mg/g for DNA-rGO- Fe_3O_4 and rGO- Fe_3O_4 , respectively. However, the adsorption data does not fit well with the Freundlich isotherm model, as indicated by the low correlation coefficients obtained for both DNA-rGO- Fe_3O_4 (Fig. 5f, red line) and rGO- Fe_3O_4 (Fig. 5f, black line).

3.6. DNA-rGO-Fe₃O₄ regeneration. The regeneration of adsorbents is crucial for their practical applications because of stringent ecological and economic demands for sustainability (Zhu et al., 2013). A 1 mM EDTA was used for regeneration order to remove Hg²⁺. The DNA-rGO-Fe₃O₄ were collected with a magnet. Figure S5a shows that the fluorescence shifted back to the background level in five cycles, whereas Fig. S5b indicates that the removal efficiency of Hg²⁺ reached over 75% after its reuse in five cycles. The results demonstrate the good reusability of the as-prepared adsorbent.

3.7. Detection and removal of Hg²⁺ from water sample. Real water samples were collected from the lake in the old summer palace to evaluate whether the new method developed here was suitable for practical applications (Ai et al., 2009). Given that these water samples excluded Hg²⁺ as determined by ICP-MS, Hg²⁺ was deliberately added to simulate the contaminated water. The recovery results, which were obtained using the previously described DNA-rGO-Fe₃O₄ detection system, are shown in Table 1. The recovery rates of the detection system ranged from 101% to 106%, and the relative standard deviation was between 3% and 6%, definitely demonstrating the accuracy and reliability of the present and actual detection method for mercury.

The removal experiments were conducted by adding Hg²⁺ to the real water samples, and the removal efficiency was evaluated by adding 5 mg DNA-rGO-Fe₃O₄. The results (Fig. S4) showed that these real water samples minimally interfere with the performance of DNA-rGO-Fe₃O₄, suggesting that this new adsorbent was suitable for the removal of Hg²⁺ from water samples.

Finally, simultaneous experiments were conducted by adding Hg²⁺ to 10 mL real water samples, and 5 mg DNA-rGO-Fe₃O₄ were then added to the samples in 5 µg/mL

Hg²⁺ concentrations. After being stirred for 170 min, the adsorbed mercury ions were separated from the mixture with permanent hand-held magnets. The supernatants were then collected and added with DNA-rGO-Fe₃O₄ (50 nM DNA) and 2×SYBR Green I to detect the concentrations. Supernatants were also determined by ICP-MS in the previously described DNA-rGO-Fe₃O₄ detection system. Results, which indicate good accuracy, are shown in Table S4.

4. Conclusion

In conclusion, the DNA-rGO-Fe₃O₄ composite was synthesized through a chemical route, which can effectively detect and remove Hg²⁺ both in buffers and in real water samples. The sensor showed high sensitivity and selectivity for detection considering that the limit detection was low at 0.82 ng/mL. The DNA-rGO-Fe₃O₄ similarly indicates its highly selective adsorption capacity for Hg²⁺. The adsorbent is stable and environmentally friendly with a high Hg²⁺ adsorption capacity of 180.8 mg/g. The method exhibits good regeneration, as well as high sensitivity and selectivity. Thus, achieving mercury detection and removal in natural water samples is possible, and the potentially interfering ions can be identified.

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378 **Acknowledgements.** This work was supported by the Tsinghua University Initiative

379 Scientific Research Program (No.2014z21028) and National Basic Research of China

380 (Grant Nos. 2015CB932500 and 2013CB632702) and NSF of China (Grant No.

381 51302141). H. W. acknowledges the support from the 1000 Youth Talents Plan of

382 China.

383 **Author Contributions.** Y.L. developed the concept. Y.L., X.W. designed and

384 performed the experiments and analyzed the data. Y.L. wrote the manuscript and all of

385 the authors commented on the manuscript. Y.L. and H.W. directed the research.

386 **Additional information.** The authors declare no competing financial interests.

Figure 1 (a) DNA sequence of Amino-Hg-DNA and fluorescence signal generation for Hg^{2+} detection. The 5'-end is modified with an amino group for rGO-Fe₃O₄ attachment. (b) Preparation of DNA- rGO-Fe₃O₄ and interaction with Hg^{2+} and SYBR Green I produces a fluorescence change. (c) Chemical reaction schemes of Amino-Hg-DNA with PASE. (d) Chemical reaction schemes of Hg^{2+} binding with thymine base pairs.

Figure 2| Characterization of Fe_3O_4 MNPs and $\text{rGO-Fe}_3\text{O}_4$. (a) SEM image of $\text{rGO-Fe}_3\text{O}_4$. (b) XRD plots. (c) Magnetic properties.

Figure 3| (a) Fluorescence spectra of SYBR Green I and DNA- rGO- Fe_3O_4 based system in the presence or absence of Hg^{2+} . (b) The spectra of fluorescence turn-on detection of Hg^{2+} from 0 to 100 ng/mL using SGI-DNA- rGO- Fe_3O_4 . (c) Calibrated curve for the detection of Hg^{2+} . (d) The liner results for detection of Hg^{2+} .

Figure 4 | F/F₀ of SGI-DNA-rGO-Fe₃O₄ complex upon the addition of different metal ions (100 ng/mL for Hg²⁺; 500 ng/mL for Ag⁺, Ca²⁺, Zn²⁺, Mg²⁺, Pb²⁺, AL³⁺, K⁺, Cu²⁺). Insert: The fluorescence spectra of SGI-DNA-rGO-Fe₃O₄ complex upon the addition of different metal ions. Condition: DNA-rGO-Fe₃O₄ (50 nM DNA), 2×SYBR Green I.

Figure 5 | Effect of adsorption time on adsorption capacity: (a) plot for the adsorption of Hg^{2+} . (b) pseudo-second-order. (c) and pseudo-first-order. Adsorption isotherm fit of Hg^{2+} adsorption on $\text{rGO-Fe}_3\text{O}_4$ and $\text{DNA-rGO-Fe}_3\text{O}_4$: (d) Henry. (e) Langmuir. (f) Freundlich.

Table 1. Recovery rate in water samples (n=3, 0.5mg/mL of DNA-rGO-Fe₃O₄).

Sample	Added concentration (ng/mL)	Detected concentration (ng/mL)	Relative standard deviation (%)	Recovery rate (%)
Deionized water	5	5.25	3.23	105
	10	10.32	3.63	103.2
	15	15.37	4.11	102.5
Laker water	5	5.27	4.51	105.4
	10	10.34	3.71	103.4
	15	15.43	4.47	102.9