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Determination of iron(III) based on the fluorescence quenching of rhodamine B derivative

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ABSTRACT

A new method for determination of iron(III) has been developed using a kind of rhodamine B derivative fluorescent probe, rhodamine amide (RHA), in acidic HAc–NaAc buffer solution. In this approach, the heavy atom effect of I_3^- was applied to quench the fluorescence of RHA. When iron(III) and KI coexisted in HAc–NaAc buffer solution, iron(III) reacted with the excess KI to produce I_3^- that quenched the fluorescence of RHA through the formation of a non-fluorescence compound. The results showed that the fluorescence intensity decrease of RHA presented a good linear relationship with the iron(III) concentrations in the range from 0.5 to 5.0 μmol L^{-1} with the correlation coefficient of 0.9970, and the detection limit was 0.3 μmol L^{-1} iron(III). The approach was applied to determination of iron(III) in water samples, and the recovery was found to be from 80.7% to 100. 8%.

1. Introduction

The determination of metal ions has continually gained tremendous attention in recent two decades due to its importance in environment, biology and chemistry domains [1–5]. Among biologically important transition metal ions, iron ions play a crucial role in many biological and environmental processes. Both iron(III) deficiency and overloading induce serious disorders such as Huntington [6–8]. In water environment, iron(III) becomes another important limiting element for phytoplankton primary productivity except for the elements nitrogen, phosphorus and silicon in recent years [9–11]. The supply of iron(III) is the chemical limitation of phytoplankton growth not only throughout the equatorial Pacific but also over much of the vast South Pacific gyre [11]. Hence, it is very essential to establish accurate and simple methods for the rapid determination of iron(III) due to its important role in environment. Until now, many methods have been employed to determinate iron(III) including inductively coupled plasma mass (ICP-MS) [12,13], fluorescence [14–16], atomic absorption [17,18], colorimetry [19,20], flow injection [21,22] and electrochemical methods [23–25]. Currently, compared with these methods, fluorescence approaches have gained greater attention due to their simple equipment, rapid response, high sensitivity and easy operation [26–29]. Based on their availability, low cost, long-wavelength emission, as well as high molar absorption coefficient and quantum yield, rhodamines have already been used as fluorescent probes to determinate iron(III) in recent years [30–33]. Some rhodamine derivatives have been applied to detect iron(III) based on the on/off switch of the spirocyclic moiety mechanism [31–34]. Tong and his coworkers have reported a non-fluorescent and colorless spirocyclic rhodamine derivative which emitted strong fluorescence when its spirocyclic ring opened in the presence of iron(III) [15]; however, its low sensitivity and poor solubility in water limited its applications in aqueous solution. In this study, we developed a sensitive approach using rhodamine amide (RHA) for the determination iron(III) in acidic aqueous solution. In the proposed method, the fluorescence of RHA was quenched due to the formation of I_3^- which generated from the reaction between iron(III) and KI. The decreased fluorescence intensity of RHA showed good linear relationship with the added trace amount of iron(III).

2. Experimental

2.1. Reagents and chemicals

All chemicals for the synthesis of RHA were ordered from Sigma-Aldrich and used as received unless noted. $FeCl_3$, KI, HAc, NaAc, $ZnCl_2$, $MgCl_2$, $NiCl_2$, $CaCl_2$, $CdCl_2$, $MnCl_2$, $AlCl_3$, $PbCl_2$, $CoCl_2$, $Cr(NO_3)_3$, $CuCl_2$ and $FeSO_4$ were purchased from sinopharm chemical reagent company (Shanghai, China) and used without further purification. HAc–NaAc buffer solution (pH 3.2) was

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prepared using 0.1 mol L^{-1} HAc and proper amount of 0.1 mol L^{-1} NaAc. All aqueous solutions were prepared with pure water from a Millipore Auto pure WR600A system (Millipore Ltd. USA).

2.2. Apparatus

Fluorescence spectra were recorded using a F-4500 (Hitachi, Japan) fluorometer. All pH measurements were operated using a pH-510 (Eutech, Instruments, Singapore). Temperature was controlled using a Julabo F12-ED (Julabo Inc., Germany) refrigerated/heating circulator.

2.3. Synthesis procedure

According to the reported procedures [2], rhodamine B acid chloride could be obtained from the reaction of rhodamine B with phosphorus oxychloride. As the reported method [15], the crude acid chloride obtained from the previous step was dissolved in 60 mL acetonitrile and added dropwise to a solution dissolved 5 mL diethylenetriamine in 20 mL acetonitrile over 0.5–1.0 h in ice bath, stirred overnight at room temperature. Then, the solvent was removed under reduced pressure. Finally, the purple solid was dried and purified by a column chromatographic method (CH_2Cl_2:CH_3OH=10:1, v/v).

2.4. Fluorescence determination procedure

Different amounts of iron(III) (0.0–15.0 μmol L^{-1}) were mixed with 0.01 mol L^{-1} KI and stayed in dark for 10 min. The same volume of RHA (10.0 μmol L^{-1}) solution and the suitable volume of HAc–NaAc buffer solution (pH 3.2) were added to the previous solution, and kept the same final volume. Then, the prepared solution was put in a dark place for 10 min. Finally, the fluorescence intensity of the solution was measured at 575 nm with excitation at 510 nm, and a slit width of 5 nm for both excitation and emission. The calibration curve was performed using the relative fluorescence intensity ($(F_0-F)/F_0$) of RHA and iron(III) concentrations. F_0 and F are the fluorescence intensities of RHA at 575 nm in the absence and the presence of iron(III), respectively.

Wastewater, tap water and lake water samples were collected from the Xiamen University. The water samples were filtered using 0.45 μm filter membranes before used. 450 μL water samples were mixed with 50 μL 0.02 mol L^{-1} KI solution and stored in a dark place for 10 min. Then, 500 μL of 10 μmol L^{-1} RHA was added and the final solution (total 1.0 mL) was kept in a dark place for 10 min. Finally, the fluorescence intensity of the solution was measured at 575 nm with excitation at 510 nm, and a slit width of 5 nm for both excitation and emission.

3. Results and discussion

3.1. Optical characteristics of RHA and possible mechanism

The fluorescence characteristics of RHA in ethanol and HAc–NaAc solution (pH 3.2) were studied. As shown in Fig. 1a, non-fluorescence in ethanol, but strong fluorescence in acidic HAc–NaAc solution [15] could be found for RHA since the molecular structure of RHA was changed from the spirocyclic form to the opening state (Fig. 1b). Interestingly, the fluorescence emission of RHA could obviously be quenched only in the synchronous presence of iron(III) and KI in HAc–NaAc solution (Fig. 2a4). In order to explain this phenomenon, comparison experiments were carried on. As shown in Fig. 2a2 and a3, the results revealed that there were no obvious fluorescence intensity change of RHA when it reacted with iron(III) or KI, respectively. The synergetic effect of iron(III) and KI was quite important in the fluorescence quenching of RHA, which may lead the inner molecular charge transfer of RHA [35]. Therefore, the quenching mechanism of RHA in HAc–NaAc buffer solution might be considered as the description as shown in Fig. 2b. I_3^- generated between iron(III) and the excess KI, could be reacted with RHA to form its ionic compound (Fig. 2b) resulting in the quenching of the RHA fluorescence due to the heavy atom effect of iodine atom [36].

3.2. Optimization of the analytical procedures

3.2.1. Effect of pH

Generally, pH of solution affects the fluorescence characteristics of RHA. The fluorescence intensity of RHA decreased greatly in pH ranged from 3.0 to 4.0 as shown in Fig. 3. We could find that the change of fluorescence intensity of RHA was going placid with increasing pH, especially when pH was above 4.5 (Fig. S1 inset). This phenomenon could be ascribed to the structure transformation of RHA as described in Fig. 1. However, the relative fluorescence intensity ($(F_0-F)/F_0$) of RHA was kept constant when the pH was above 3.4 (Fig. 3).Under the consideration of stability and sensitivity, pH 3.2 HAc–NaAc solution was selected for further experiments.

3.2.2. Effect of temperature

Another important factor, temperature, should be taken into account in the effect of the probe fluorescence intensity, because higher temperature causes more non-radiative processes for the excited state of the probe. Thus, the temperature ranging from 5 °C to 40 °C in pH 3.2 HAc–NaAc solution was investigated to obtain optimal experimental conditions. Experiment results revealed that the fluorescence intensity of RHA decreased gradually with increasing temperature from 5 °C to 40 °C (Fig. S2). However, the relative fluorescence intensity ($(F_0-F)/F_0$) of RHA

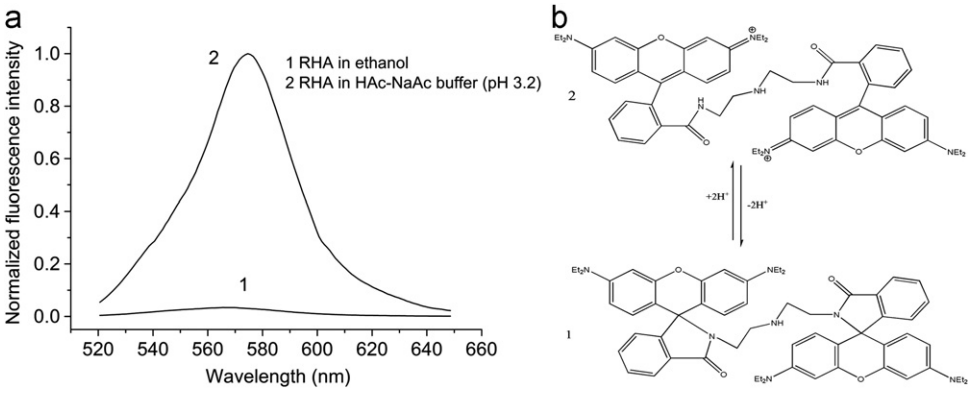

Fig. 1. Fluorescence spectra (a) and structures (b) of RHA in ethanol and HAc–NaAc solution (pH 3.2). (Excitation wavelength—510 nm).

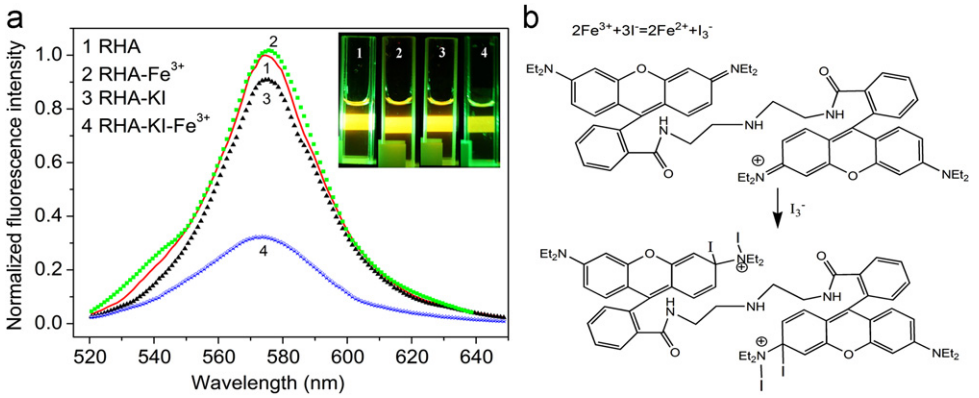

Fig. 2. (a) Fluorescence spectra of RHA before and after addition of iron(III) (1 eq) in HAc–NaAc solution (pH 3.2) and (b) Structures of RHA before and after addition of iron(III) (1 eq) in HAc–NaAc solution pH 3.2. (Excitation wavelength—510 nm).

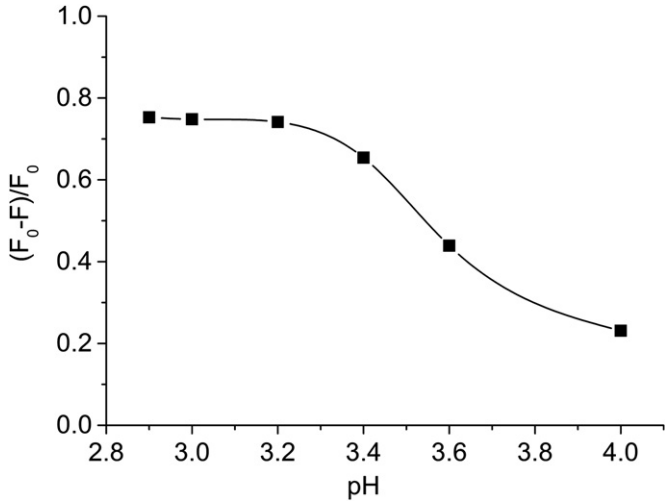

Fig. 3. Fluorescence intensity change (575 nm) of RHA after the addition of 10.0 μmol L^{-1} iron(III) in different pH HAc–NaAc solutions. (Excitation wavelength—510 nm, RHA concentration—10.0 μmol L^{-1}).

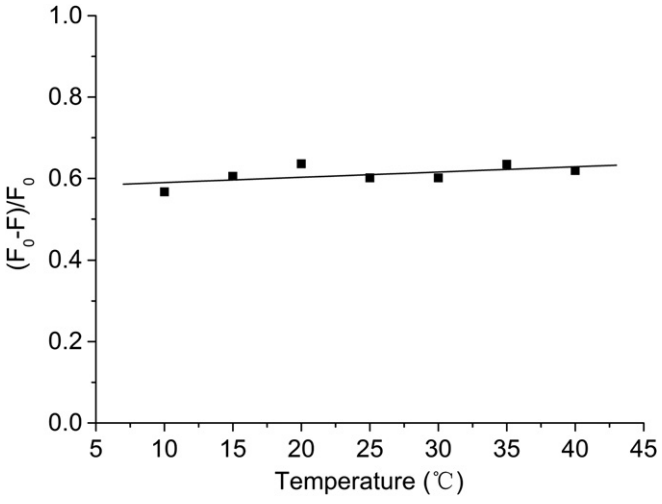

Fig. 4. Relationship between the relative fluorescence intensity of RHA and temperature in the presence of 10.0 μmol L^{-1} iron(III). (Excitation wavelength—510 nm, RHA concentration—10.0 μmol L^{-1}).

(Fig. 4) was kept constant in the presence of KI and iron(III), indicating that temperature has little influence on the relative fluorescence intensity. Using this approach, no temperature control device was necessary in the determination of iron(III).

3.2.3. *Effect of RHA concentration*

The concentration of RHA, which can affect the relative fluorescence intensity ($(F_0-F)/F_0$), was conducted in this paper and the results were shown in Fig. 5. The fluorescence intensity of RHA was increased gradually with increasing the concentration of RHA in the range from 2.0 to 30.0 μmol L^{-1}, but decreased when the concentration was above 30.0 μmol L^{-1} due to the self-absorption of RHA (Fig. S3). When the concentration of iron(III) was 10.0 μmol L^{-1}, the relative fluorescence intensity ($(F_0-F)/F_0$) of RHA decreased with increasing the concentration of RHA from 10.0 to 40.0 μmol L^{-1} (Fig. 5). The relative fluorescence intensity remained constant when the concentrations of RHA ranged from 2.0 to 8.0 μmol L^{-1}. Under the consideration of the sensitivity and the linear range to detect iron(III), 5.0 μmol L^{-1} RHA was selected for the subsequent experiments.

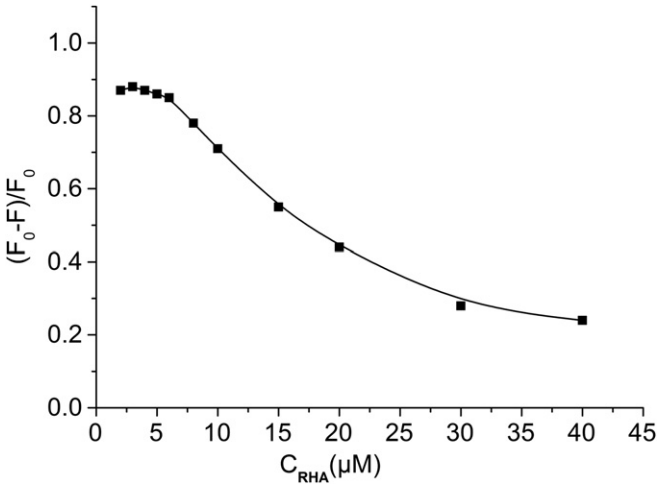

Fig. 5. Fluorescence intensity change (575 nm) of different concentrations of RHA after the addition of 10.0 μmol L^{-1} iron(III). (Excitation wavelength—510 nm).

3.2.4. *Effect of KI*

KI reacts with iron(III) to produce I_3^-, which affects the fluorescence intensity of RHA. In the experiments, different titrations of KI from 0.0 to 0.02 mol L^{-1} were conducted in Fig. S4. As shown in Fig. S4, the fluorescence intensity of RHA remained relatively unchanged with the increase of KI concentration. However, when the solution contained 5.0 μmol L^{-1} iron(III), the fluorescence

intensity of RHA decreased gradually with increasing of KI concentration (Fig. 6). Considering the reduce property of KI, 0.01 mol L^{-1} KI was chosen for further studies.

3.3. Effect of co-existing metal ions

The effects of co-existing metal ions on the relative fluorescence intensity of RHA were investigated in HAc–NaAc solution (pH 3.2). For this experiment, we selected some typical metal ions including Zn^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Cr^{3+}, Cd^{2+}, Mn^{2+}, Al^{3+}, Pb^{2+}, Co^{2+}, Cu^{2+} and Fe^{2+} as shown in Fig. 7. The addition of 5.0 μmol L^{-1} iron(III) caused obvious decrease of RHA fluorescence intensity at 575 nm (70% decreased). Comparing to other co-existing metal ions (5.0 μmol L^{-1}), about 10% decrease of RHA fluorescence intensity for Cu^{2+} and Cd^{2+} could be found. The quenching effect of Cu^{2+} and Cd^{2+} are most likely due to the electron transfer from these redox active metal ions to the excited state of RHA, which results in non-radiative decay of the excited stated [37,38]. The above results indicated that the selected system shown satisfactory selectivity in the determination of iron(III).

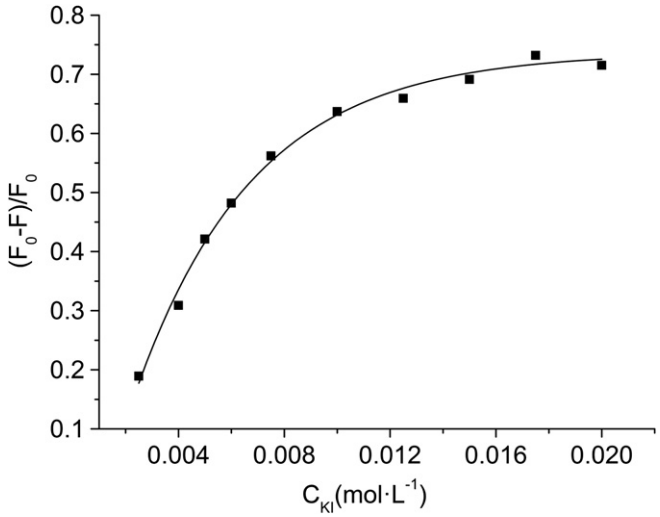

Fig. 6. Fluorescence intensity change (575 nm) of RHA after the addition of 5.0 μmol L^{-1} iron(III) in different concentrations of KI. (Excitation wavelength—510 nm, pH 3.2 HAc–NaAc solution, RHA concentration—5.0 μmol L^{-1}).

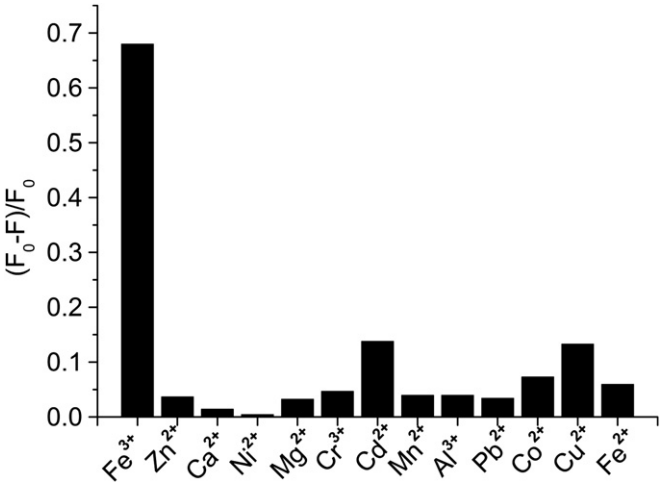

Fig. 7. Effects of co-existing cation ions (Emission wavelength—575 nm, RHA concentration—5.0 μmol L^{-1}, ions concentration—5.0 μmol L^{-1}).

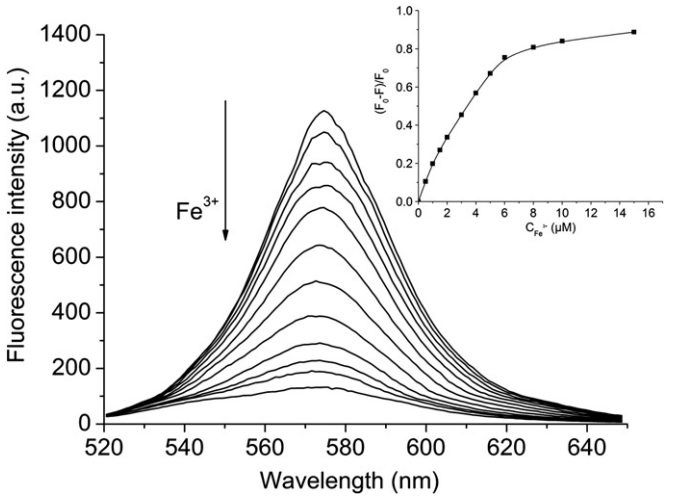

Fig. 8. Fluorescence titration spectra of RHA (5.0 μmol L^{-1}) on the addition of iron(III) (0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 8.0, 10.0, 15.0 μmol L^{-1}) in HAc–NaAc solution (pH 3.2) (Excitation wavelength—510 nm, emission wavelength—575 nm).

Table 1
Iron(III) detection in water samples using the proposed method ($n=5$).

Water samples	Detected (μmol L^{-1})	Added (μmol L^{-1})	Detected (μmol L^{-1})	RSD (%)	Recovery (%)
Lake water	0.77 ± 0.17	1.0	1.62 ± 0.10	6.0	84.6
		1.5	2.10 ± 0.07	3.3	87.8
Wastewater	0.92 ± 0.14	1.0	1.73 ± 0.04	2.3	80.7
		1.5	2.43 ± 0.12	4.9	100.8
Tap water	ND	2.0	1.76 ± 0.08	4.5	88.0
		2.5	2.42 ± 0.06	2.0	96.8

ND: not detected.

3.4. Calibration graph and analytical application

Under the optimal conditions, the calibration graph was plotted between the relative fluorescence intensity of RHA and iron(III) concentration (Fig. 8). The results indicated that the relative fluorescence intensity of RHA was proportional to the iron(III) concentration in the range from 0.5 to 5.0 μmol L^{-1}. The linear regression equation was $(F_0-F)/F_0=0.1007+0.1128C$, ($n=3$), with the correlation coefficient 0.9970. The detection limit was found to be 0.30 μmol L^{-1}. The LOQ values are 0.5 μmol L^{-1} and 10.0 μmol L^{-1}. Furthermore, the method developed was applied for the analysis of water samples and the determination results were shown in Table 1. Wastewater, tap water and lake water samples were collected from the Xiamen University, filtered and analyzed using the procedure mentioned above. None of the target ion (iron(III)) was detected in tap water. The recovery of the collected water samples was ranged from 80.7% to 100.8% as shown in Table 1. All the results of the water samples were illustrated that the developed method is feasible.

4. Conclusions

In summary, a new approach using RHA as a fluorescence quenching probe has been proposed to determine iron(III). RHA changed to its non-fluorescent ion form after the reaction with I_3^-, which yields from the reaction of iron(III) and KI in an acidic aqueous. This process results in the decrease of fluorescence intensity of RHA. It is found that the relative fluorescence intensity of RHA keeps a constant under a wide range of temperature.

Experimental results show a good linear relationship between the relative fluorescence intensity of RHA and the concentration of iron(III) in the range from 0.5 to 5.0 μmol L^{-1}. This method presents good selectivity for iron(III) and has been applied in the determination of iron(III) in water samples.

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Appendix A. Supplementary materials

Supplementary materials associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.10.078.

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