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Simultaneous detection of trace toxic metal ions, Pb^{2+} and Ag^{+}, in water and food using a novel single-labeled fluorescent oligonucleotide probe

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ABSTRACT

Owing to the high toxicity of lead (II) (Pb^{2+}) and silver (I) ions (Ag^{+}) to aquicolous organisms, it is highly desirable to develop a sensitive method for the simultaneous detection of Pb^{2+} and Ag^{+}. In this work, a novel and sensitive single-labeled fluorescent oligonucleotide (OND) probe is designed to simultaneously detect based on the specific complexation of Ag^{+} to cytosines, the special induction capacity of Pb^{2+} to guanine-rich OND to form G-quadruplex and the inherent quenching ability of G-quadruplex to the hexachloro fluorescein (HEX). The Ag^{+}-induced hairpin-link structure makes HEX labeled at the 5′-termini close to the Pb^{2+}-induced G-quadruplex connected at the 3′-terminin, resulting in a remarkable fluorescence quenching owing to photoinduced electron transfer (PET) process from G-quadruplex to HEX. At 298 K, the apparent associating constant between them is 1.85×10^{8} (L/mol). Using this system, we can simultaneously detect the Pb^{2+} and Ag^{+} over the linear response range of 1–100 nmol/L with a detection limits of 96 pmol/L and 21 pmol/L, respectively. Through the assay in real samples, it is known that this system could be applied to accurately monitor the trace Pb^{2+} and Ag^{+} in aqueous solution.

1. Introduction

With the rapid development of modern industries, some toxic heavy metal ions, such as Pb^{2+}, Cu^{2+}, $Hg^{2+}$and Ag^{+}, are increasingly emitted into the surrounding as environmental contaminant in recent decades [1]. These poisonous metal ions exist in environment primarily in the form of cationics and can be accumulated millions of times by fish and shellfish at very light low concentrations. Owing to their non-degradable or non-destroyed and toxicity, they have posed a much serious harm to the central nervous system, kidney, liver, bone [2], and serious illness, such as various cancer and cardiovascular diseases [3,4]. In particular, it is estimated that the number of deaths annually from infection with Pb^{2+} is up to 143, 000 [5]. And Ag^{+} often makes sulfhydryl enzymes and contain imidazole, amine and carboxyl groups of different compounds inactivate[6]. Up to now, numerous traditional techniques, including inductively coupled plasma-mass spectrometry, electrochemical analysis, atomic absorption spectrophotometry, fluorescence emission spectroscopy and so forth, are available for heavy metal ion detection in biological or environmental samples [7–13]. Of all these approaches, the fluorescence spectrum is widely used due to simple operation, high selectivity, sensitivity and the ability to provide real-time monitor [14–21]. Moreover, numerous heavy metal ions generally coexist in actual samples and the simultaneous detection is of particular significant. Fortunately, a variety of techniques, such as electroanalytical [22,23], multichannel/multidimensional [24,25] and probe array techniques [26–28], have shown such capability and have been applied for detection and discrimination of multiple analytes. Therefore, it is still highly desired for a new simple, rapid and sensitive detection means of simultaneous tracking these heavy metal ions, particularly in aqueous environment.

In the previous work, many oligonucleotide probes have been reported for Ag^{+} detection according to the interaction between Ag^{+} and cytosine [29,30]. However, many of these methods can only be used in single Pb^{2+} or Ag^{+} with complicated operating steps [31–36]. In our work, we developed a novel method for simultaneous detection of trace Pb^{2+} and Ag^{+} in aqueous solution. This method shows excellent anti-interference characteristic and can be applied not only to selectively monitor the individual Pb^{2+} or Ag^{+}, but their mixtures simultaneously, with sensitivity and selectivity satisfying the Chinese wastewater discharge standard concentrations [37].

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2. Materials and methods

2.1. Chemicals and samples

The single-labeled fluorescent OND probe, whose nucleotide sequence is 5′-HEX-CCCTCCTTCCCTTCCTTTTCC AACCCAACCACCGGTTGGTGTGGTTGG-3′, was synthesized from Sangon Biotech Co. Ltd. (Shanghai, China). DNA concentration was determined by UV–vis spectroscopy. MOPS (3-(N-Morpholino)-propanesulfonic acid) was obtained from Sigma-Aldrich Inc. (Shanghai, China). $NaNO_3$, KF, NaCl, $AgNO_3$, $Pb(NO_3)_2$, $Ca(NO_3)_2$, $CoSO_4$, $Mg(NO_3)_2$, $Mn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Hg(NO3)_2$, $ZnSO_4$, $Cr(NO_3)_3$ and $Fe_2(SO_4)_3$ were used as received without further purification. All the HEX-OND probe solutions (20.0 nmol/L), Pb^{2+} solutions and Ag^+ solutions were dissolved in 10.0 mmol/L MOPS buffer (containing 0.40 mol/L $NaNO_3$, pH 6.0). The ultrapure water (18.2 MΩ cm) was obtained from a Millipore ultrapure water system. Tap water, river water and wastewater samples were gathered from a household water pipe in our lab, Wei River near Xi'an and wastewater storage tank respectively. "Da-Hong-Pao" tea (Tian-Yi Tea Culture Research Center, Wuyishan, Fujian) and "Xi-Jun-Zhu" wild yellow mushroom (Qinghai West Infanta Biological Technology Co. LTD, Xining, Qinghai) samples were purchased from a supermarket nearby.

2.2. Physical measurements

All fluorescence assays were acquired with a Hitachi F-4500 fluorescence spectrophotometer. 10 μL of 1.0 mmol/L fluorescent HEX-OND probe was prepared in 490 μL of MOPS buffer and hold for 10 min at 95 °C. Then the mixture was gradually cooled and incubated overnight at 25 °C. The incubated solution was then transferred into a the quartz cells and the fluorescent emission were recorded over the range of 540–630 nm upon excitation at 521 nm at 25 °C. Both the width of excitation and emission slit were 10 nm. The resulting solution was 20 mol/L fluorescent HEX-OND probe, NaNO3 (0.40 mol/L) and MOPS (10.0 mmol/L, pH 6.0). After mixing, 1.0 μL Pb^{2+} solutions with various concentrations under a given concentration of Ag^+ (when Pb^{2+} were detected) or 1.0 μL Ag^+ solutions with variable concentrations under a given concentration of Pb^{2+} (when Ag^+ were detected) were separately added into the resulting solution and their fluorescent assay procedures were recorded under the same conditions. All the UV/Vis spectra were performed on a UV-2450 spectrophotometer (Shimadzu).

2.3. Application

To confirm the application of this strategy in real sample, we measured the Pb^{2+} and Ag^+ in water samples (wastewater, tap water and river water) and two food samples (tea and mushroom).

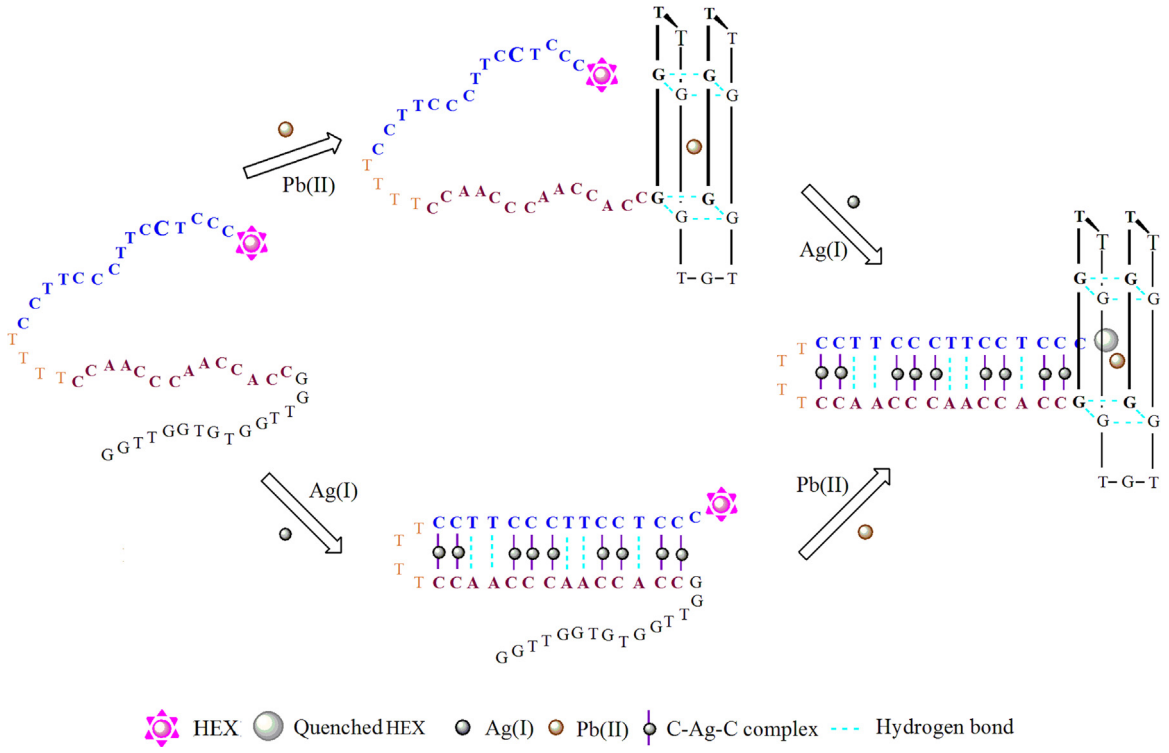
For the water sample detection, all water samples before fluorescence spectra assays were conducted were filtered through a 0.22 μm membrane. The fluorescent HEX-OND probe dissolved in 400 μL of MOPS buffer was first heated for 10 min at 95 °C. Then the solution was cooled and incubated overnight at 25 °C. After that, 100 μL of various water samples were separately added. The total volume of the resulting solution was 500 μL containing 20.0 nmol/L HEX-OND probes, 0.40 mol/L NaNO3 and MOPS (10.0 mmol/L, pH 6.0). The fluorescence spectra were recorded under the optimum condition.

For the food samples (tea and mushroom) detection, the details of the method were described in our previous study [33].

3. Results and discussion

3.1. Fluorescence quenching of HEX-OND probe

As illustrated in Scheme 1, a G-rich OND(5′-GGTTGGTGTGGTTGG-3′) is connected with a C-rich OND(5′-CCCTCCTTCCCTTCCTTTTCCAACCCAACCACC-3′) and HEX labeled, a fluorescenin-base dye, at its 5′-terminal. This OND probe is based on the specific complexation of Ag^+ to cytosines, the spe-



Scheme 1. Schematic diagram to illustrate the single-labeled florescent OND probe for the simultaneous detection of trace Pb(II) and Ag(I) ions.