Fe(II)-DTPA 착물의 촉매작용을 이용한 루미놀 화학발광 시스템의 선택적 Fe(II) 정량

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A Selective and Sensitive Determination Method of Fe(II) ion using DTPA in Luminol–H₂O₂ System

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Abstract

A sensitive and selective determination method of Fe(II) ion by luminol–H₂O₂ system using a chelating reagent has been presented. A metal ion–chelating ligand complex such as Fe(II)–diethylenetriamine pentaacetic acid (DTPA) produced higher chemiluminescence (CL) intensity as well as longer lifetime in luminol–H₂O₂ system than metal exist as free ions. Furthermore, the catalytic activity of Cu(II) and Pb (II) complexes with chelating reagents in luminol–H₂O₂ system was lost since chelating reagents act as a masking agent although free Cu(II) and Pb(II) ions have high catalytic activity. On the optimized conditions, the calibration curve of Fe(II) ion was linear over the range from 1.0×10⁻⁷ to 2.0×10⁻⁵ M with correlation coefficient of 0.996. The detection limit was calculated to be 4.0×10⁻⁸ M.

Keywords: Fe(II) Ion, Liminol, Chemiluminescence, DTPA

1. Introduction

Determination of a metal ion in trace levels is possible by chemiluminescence (CL) with simple and inexpensive instrumentation, since no external light source is needed. In the presence of excess luminol and hydrogen peroxide, CL intensity is directly proportional to metal ion concentration over several orders of magnitude. The methods is based on the property of transition metal ions to catalyze the oxidation of hydrogen peroxide towards the formation reactive oxygen species, mostly ‘OH and O₂’− [1–3]. A serous obstacle of the luminol reaction is inherently lack of selectivity, thus it has been used as detection methods for ion-exchange separation [4] and capillary electrophoresis [5] of metal ions. In this study, a luminol–H₂O₂ system that enables the selective and sensitive determination of a Fe(II) ion using a chelating reagent is presented. When Fe(II) ion makes complex with DTPA, it offers better signal response
with reference to time stability, CL intensity, signal reproducibility as well as selectivity.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. Doubly deionized (DI) water was used throughout. A 2 mM of luminol standard solution (Sigma–Aldrich) was prepared by dissolving in 10 mM of NaOH solution and stored at 4°C. A DTPA (Junsei Chemical Co.) stock solution, 5 mM, was prepared using 1 mM of NaOH solution. And 0.1 M borate buffer was prepared by dissolving H$_3$BO$_3$ (Sigma–Aldrich) in DI water and pH of the buffer solutions were adjusted with NaOH solution. All metal ion solutions were prepared from either nitrate or chloride salts.

2.2. Apparatus and procedures

CL measurement were carried out on a Model F–4500 spectrofluorimeter (Hitachi, Japan) with keeping the lamp off and using only the photomultiplier (PMT) of the apparatus. The high voltage for the PMT tube was set as 700 V and the slit width of emission monochromator was 5 nm. Light producing reactions were carried out in a 1×1 cm quartz cell placed in the spectrofluorimeter cell holder. Fe(II) ion, DTPA, borate buffer and luminol solutions were introduced to the quartz cell. And then CL intensity at 430 nm was measured for 10–19 seconds after H$_2$O$_2$ solution was injected to initiate the CL reaction. Average values of the obtained CL intensity with 10 data (from 10 to 19 sec) of 4 measurements were drawn in each graph.

3. Results and Discussion

3.1. Ligand specificity with Fe(II) ions

The CL spectra (Fig. 1) show the catalytic activity of Fe(II) ion complexed with different chelating ligands in luminol–H$_2$O$_2$ system. Ethylenediamine tetraacetate (EDTA), ethylenediamine diacetate (EDDA) and DTPA were used as chelating ligands. Like free Fe(II) ion, EDTA and EDDA ligands did not induce detectable CL signals. Only Fe(II)–DTPA complex showed strong catalytic effect in this system. Presumably, catalytic activity is deeply related with ligand structure and coordination number of chelating ligand.
3.2. Enhanced selectivity of a metal ion–DTPA complex

Various metal ions were applied to DTPA ligand to check catalytic selectivity, and the result are shown in Fig. 2. DTPA deactivated catalytic effect of a metal ion in the luminol–H$_2$O$_2$ system except for Fe(II) and Cr(III). Furthermore, the CL intensity of Fe(II)–DTPA complex in the luminol–H$_2$O$_2$ system is over 100 times higher than other metal ion–DTPA complexes excluding Cr(III).

3.3. Calibration curve

The effects of H$_2$O$_2$ concentration, pH, buffers, and concentration of DTPA were investigated and optimized (data not shown). On the optimized conditions, a calibration curve of CL intensity against Fe(II) ion concentration was shown in Fig. 3. The CL intensity is linear over the range from $1.0 \times 10^{-7}$ to $2.0 \times 10^{-5}$ M with correlation coefficient of 0.996. In this range, reproducibility (RSD) was 2.16% and detection limit was calculated to be $4.0 \times 10^{-8}$. 

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**Fig. 1.** Ligand specificity in luminol–H$_2$O$_2$ system with Fe(II) ion catalysis: [luminol], 0.4 mM; [H$_2$O$_2$], 0.2 mM; [Fe$^{2+}$], 0.01 mM; [ligand], 0.1 mM; pH, 13.

**Fig. 2.** Enhanced selectivity of metal ion–DTPA complex in luminol–H$_2$O$_2$ system: [luminol], 0.4 mM; [H$_2$O$_2$], 0.2 mM; [metal ion], 0.01 mM; pH, 13 and then added (a) DI water, (b) [DTPA], 0.1 mM each other.
Fig. 3. Calibration curve of Fe(Ⅱ) ion concentration: [luminol], 0.4 mM; [H$_2$O$_2$], 0.2 mM; [DTPA], 0.1 mM; pH, 13; [borate buffer], 20 mM.

4. Conclusion

A selective determination method of Fe(Ⅱ) ion using a chelating reagent has been described. Fe(Ⅱ)−DTPA produced high CL intensity as well as longer lifetime in luminol−H$_2$O$_2$ system. The proposed method can be used efficiently for field analysis using a miniaturized device such as a microfluidic chip without separation.

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