An Optical Sensing Film for Fe(III) Determination Based on 1,1'-diethyl 2,2'-cyanine Iodide Immobilized in Nafion Film

K. Kajsanthia, J. Wittayakun, S. Prayoonpokarach

Abstract—An optical chemical sensing film based on immobilizing of 1,1'-diethyl 2,2'-cyanine (pseudocyanine iodide) in nafion film was developed for the determination of Fe(III). The sensing film was homogeneous, transparent, and mechanically stable. Decrease of the absorbance measured at 518 nm was observed when the sensing film was immersed in a solution of Fe(III). The optimum response of the sensing film to Fe(III) was obtained in a solution with pH 4.0. Linear calibration curve over an Fe(III) concentration range of 1-30 ppm with a limit of detection of 0.71 ppm was obtained. Cd(II) is the major interference. The sensing film exhibited good stability for 2 months and high reproducibility. The proposed method was applied for the determination of Fe(III) in water samples with satisfactory results.

Keywords—iron(III), nafion, optical sensing film, pseudocyanine iodide

I. INTRODUCTION

IRON is one of the heavy metals found in environmental samples. It is an essential element for the formation of hemoglobin of red blood cells and plays an important role in the storage and transportation of oxygen to tissues. However, damaging health effects can be observed when high concentration is intake. Early symptoms of iron overload or hemochromatosis include fatigue, tissue damage, headache and irritability. Therefore, the concentration of iron should be monitored periodically. World health organization (WHO) recommended the limit of Fe (III) in drinking water to be < 0.3 mg/L and concentration of 1-3 mg/L can be accepted for people drinking anarobic well water [1].

Iron can be determined by several techniques, for example atomic absorption spectrometry (AAS) with a detection limit 6.5 × 10^{-5} \mu g/L [2], flow injection spectrometry with a detection limit 0.30 \mu g/L [3], and high performance liquid chromatography with a detection limit 7.8 × 10^{-6} \mu g/L [4]. All of these methods gave low detection limits, but the methods require relatively expensive instruments and a skilled operator. Optical chemical sensors have been developed as the alternative for the determination of heavy metals. Many advantages of the optical chemical sensors include less expensive instrument, high sensitivity and selectivity, small size and easy to use.

In recent years, there are many reports on optical chemical sensors for the determination of Fe(III) based on immobilization of the synthesized bis(7-methoxybenzofuran-2-il)ketoxime in PVC and ethyl cellulose [5] 2,4-dinitroresocinol in XAD-7 [6], 2-(2'-hydroxy-phenyl)-4(3H)-quinazolinone in PVC [7], pyoverdin in controlled pore glass [8], 4-(2-furylmethylene)-2-phenyl-5-oxazolone in PVC [9] and anthocyanin in grape skin in glass slide [10].

![Fig. 1 Chemical structure of 1,1'-diethyl 2,2'-cyanine iodide.](image)

The search for new selective sensing reagents for Fe(III) has led to a continuous development of the sensors. In this research, 1,1'-diethyl 2,2'-cyanine iodide (pseudocyanine iodide, Fig.1.) was first investigated for its reactivity to Fe(III). The chosen dye was immobilized in nafion film. The developed optical chemical sensing film was evaluated for its performance characteristics and was employed in an analysis of a real water sample.

II. EXPERIMENTAL

A. Reagents

All of the chemicals used were of analytical reagent grade. Doubly distilled water was used throughout. Fe(III) solutions were prepared from a standard Fe(III) solution (1000 mg/L,BDH) with desired dilution. Buffer solutions were prepared from phosphoric acid (99.00%, Fluka), disodium hydrogen phosphate (99.00%, Qrect™) and sodium dihydrogen phosphate (99.00%, Qrect™).

B. Preparation of Sensing Films

Sensing films were prepared by dissolving pseudocyanine iodide (97.00%, Aldrich) in 2 mL of 5% nafion solution (Fluka) with 60 min sonication. The cocktail solution was cast to a size of 1.0 x 1.0 cm on a rectangular transparent film and dried at room temperature for 24 h. The films were kept in a desiccator.

C. Measurement Procedures

Absorbance measurement was made using CHEM4-Vis-
fiber spectrometer (USB 4000, Ocean optics). Measurement of pH was carried out with a digital pH meter (DELTA 320, Mettler Toledo). An atomic absorption spectrometer (AAnalyst 100, Perkin-Elmer) was used for determination of Fe(III) in water samples. For measurement with sensing films, a sensing film was immersed in a cuvette containing 2 mL of a sample solution with continuous stirring.

**D. Water Sample Preparation**

Water samples were collected from a reservoir and piped water supply located in Suranaree University of Technology (SUT), Nakhon Ratchasima, Thailand. The water samples were filtered and stored in polypropylene containers at 4.0 °C. For the measurement with the sensing film, the water samples were filtered and pH of the sample solutions was adjusted to 4.0 with a buffer solution. The determination of Fe(III) in water samples with the atomic absorption spectrometer was done according to a reference method [11].

**III. RESULTS AND DISCUSSION**

**A. Response of the Sensing Film to Fe(III)**

Nafion was used as a supporting matrix for pseudocyanine iodide due to its sulfonate groups can electrostatically interact with the positive charge of the dye. Several properties of nafion including hydrophobicity, resistance to most solvents, oxidants and bases and permeability for many cations are beneficial for sensor applications. Absorption spectra of the sensing film and the sensing film in Fe(III) solution are shown in Fig.2. Maximum absorption of the dye was at 518 nm and the absorbance was decreased when the sensing film was exposed to Fe(III). The decrease in the absorbance signal linearly correlates to the concentration of Fe(III).

Fig. 3 shows kinetically response of the sensing film submerged in solutions with different Fe(III) concentrations.

**B. Effect of pH**

Effect of the pH on the response of the sensing film to Fe(III) was investigated over a pH range of 2 – 8 using a solution containing 20 ppm of Fe(III) in phosphate buffer. Maximum response was obtained at pH 4.0 as shown in Fig. 4. At pH > 4.0, response signals decreased because Fe(III)-precipitates could be formed by a hydrolysis reaction of Fe(III) in an aqueous solution with higher pH. Lower response signals were also obtained at pH < 4.0 due to the protonation of the sensing reagent. Thus, a pH of 4.0 was used for further study.

**C. Calibration**

A linear calibration, \( \Delta A = 0.0043C_{\text{Fe(III)}} + 0.007 \) with \( r^2 = 0.9990 \) was obtained with an Fe(III) concentration range of 1 – 30 ppm. Detection limit, based on a concentration corresponding to the three times standard deviation of the blank signal, was found to be 0.71 ppm.

**D. Regeneration and Lifetime Studies**

Solutions of HCl and ethylenediaminetetraacetic acid (EDTA) were tested for their ability to regenerate the sensing film. It was found that 0.1 M HCl could strip Fe(III) out of the sensing film within 30 s. The sensing film could be reused for more than 30 times and the calculated R.S.D. was 2.84% based on the responses of the sensing film to 20 ppm Fe(III) solution.
The sensing film exhibited good stability over two months with the calculated R.S.D. of 3.12% based on the tested with 20 ppm Fe(III) solution.

<table>
<thead>
<tr>
<th>Ion</th>
<th>% Error</th>
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<tbody>
<tr>
<td>Cu(II), Fe(II)</td>
<td>+0.13</td>
</tr>
<tr>
<td>Ni(II), K(I)</td>
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<tr>
<td>Co(II)</td>
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<td>Mg(II)</td>
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<td>Mn(II)</td>
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<tr>
<td>Cr(II)</td>
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<tr>
<td>Cd(II)</td>
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<tr>
<td>Ca(II), Na(II)</td>
<td>+0.12</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>+4.80</td>
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</tbody>
</table>

The reported values are means of three replicate measurements.

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REFERENCES

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