

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 anaerobic well water [1].

Iron can be determined by several techniques, for example atomic absorption spectrometry (AAS) with a detection limit 6.5×10^{-5} $\mu\text{g/L}$ [2], flow injection spectrometry with a detection limit 0.30 $\mu\text{g/L}$ [3], and high performance liquid chromatography with a detection limit 7.8×10^{-6} $\mu\text{g/L}$ [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.

K. Kajsanthia, J. Wittayakun and S. Prayoonpokarach are with Material Chemistry Research Group, School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand (email:kanlayanee_k@hotmail.com, jatuporn@sut.ac.th, sanchaip@sut.ac.th).

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-yl)ketoxime in PVC and ethyl cellulose [5] 2,4-dinitrospresocinol 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].

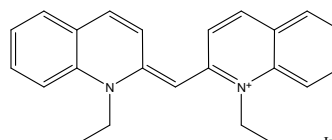


Fig. 1 Chemical structure of 1,1'- diethyl 2,2'-cyanine iodide.

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%, QrectTM) and sodium dihydrogen phosphate (99.00%, QrectTM).

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 \times 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 (AAAnalyst 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].

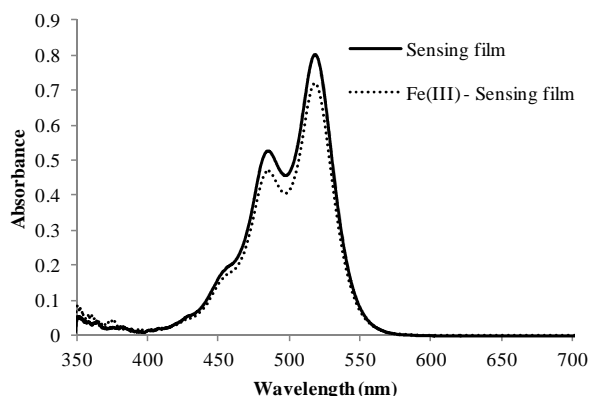


Fig. 2 Absorption spectra of the sensing film in buffer and in 20 ppm Fe(III) solution. Phosphate buffer pH 4.0 was used as a blank

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.

An absorbance difference, ΔA , was calculated by subtraction of the absorbance of the sensing film in Fe(III) solution from the absorbance of the sensing film in a buffer.

The absorbance approached a plateau in less than 1 min for 20 and 30 ppm Fe(III) solutions and the signals were relatively

stable after that. It took ~ 1 min for the signal to reach the plateau for the solution with 10 ppm Fe(III). The response time of the sensing film to Fe(III) was controlled by diffusion process and the rate of complex formation. Therefore, the time for absorbance measurement was chosen to be 1 min.

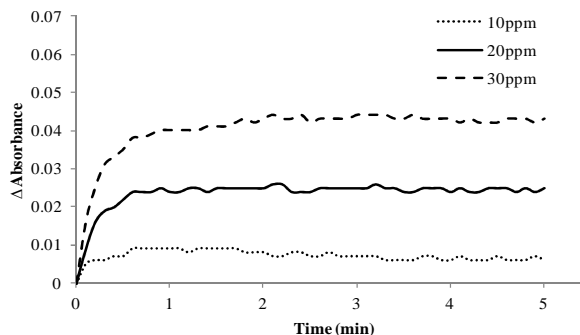


Fig. 3 Time profile of the response of the sensing film with various Fe (III) concentrations

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.

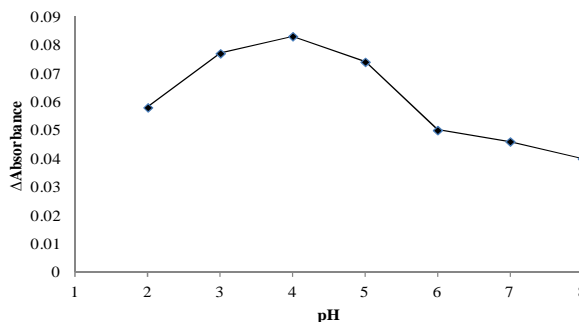


Fig. 4 Effect of pH on the response of the sensing film to Fe(III)

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 I
INTERFERENCE STUDY AT 1: 1 MOLAR RATIO OF FOREIGN ION:Fe(III)

Ion	% Error ^a
Cu(II), Fe(II)	+0.13
Ni(II), K(I)	+0.06
Co(II)	+0.10
Mg(II)	+0.03
Mn(II)	+0.48
Cr(II)	+0.51
Cd(II)	+5.34
Ca(II), Na(II)	+0.12
Zn(II)	+4.80

^a%Error = $(\Delta A_{Fe(III), ion} - \Delta A_{Fe(III)}) / \Delta A_{Fe(III)}$, where $\Delta A_{Fe(III), ion}$ is the absorbance difference of the sensing film in a solution of Fe(III) mixed with the foreign ion and $\Delta A_{Fe(III)}$ is the absorbance difference of the sensing film in a solution of Fe(III) only.

E. Effect of Foreign Ions

The effect of interference ions on the determination of Fe(III) was investigated at the optimum condition for Fe(III) by measuring the absorbance difference at 518 nm of the sensing film in a solution of Fe(III) or in a solution of Fe(III) mixed with foreign ion at the molar ratio of 1: 1. Fe(III) concentration and the foreign ions concentration were 3.58×10^{-4} M. The results are summarized in Table I. The ion ratio that exhibits an error of less than $\pm 5\%$ is considered as tolerated for the analysis. Cd(II) interfered significantly and removal of this ion should be concerned before the analysis with the sensing film.

F. Water Sample Analysis

To evaluate the applicability of the sensing films, analysis of real samples was performed with water samples collected from a water reservoir and tap water located at SUT. The results are summarized in Table II.

The results obtained from the proposed method agreed well with those obtained from the AAS method.

IV. CONCLUSION

We have presented the simple method for Fe(III) determination using the developed optical chemical sensing film based on immobilization of pseudocyanine in nafion film.

The sensing film has many advantages including simple preparation, short response time, high reproducibility and stability and regenerable capability. The proposed method provided satisfied results on the analysis of the real water samples.

TABLE II
DETERMINATION OF Fe(III) IN THE WATER SAMPLE^a

Sample	Fe(III) added (ppm)	Proposed method		AAS method	
		Fe(III) found (ppm)	Recovery (%)	Fe(III) found (ppm)	Recovery (%)
SUT water reservoir	0	ND ^b	-	ND	-
	5.00	4.98	99.5	5.51	108.3
Tap water	10.00	10.07	100.8	10.76	108.3
	0	ND	-	ND	-
	5.00	5.26	102.4	5.27	101.8
	10.00	10.06	99.2	10.57	103.9
	15.00	15.55	102.7	15.71	103.6

^aThe reported values are means of three replicate measurements.

^bND: not detected

ACKNOWLEDGMENT

The authors are thankful for Science Achievement Scholarship of Thailand (SAST) and Suranaree University of Technology for the financial support of this work.

REFERENCES

- [1] WHO. *Iron in drinking-water. Background document for preparation of WHO guidelines for drinking-water quality*. Geneva: WHO Press, Vol. 1, 2008, pp. 390-391.
- [2] H. Bag, M. Lale and A. R. Turker, "Determination of iron and nickel by flame atomic absorption spectrophotometry after preconcentration on saccharomycescerevisiae immobilized sepiolite," *Talanta*. Vol. 47, 1998, pp. 689-696.
- [3] A. Asan, M. Andac and I. Isildak, "Flow injection spectrofluorimetric determination of iron(III) in water using salicylic acid," *Chemical Papers*. Vol. 64 (4), 2010, pp. 424-428.
- [4] T. Makino, K. Nakamura and K. Takahara, "A high-performance liquid immunoaffinity chromatography method for determining transferrin-bound iron in serum," *Clinica Chimica Acta*. Vol. 412, 2011, pp. 914-919.
- [5] O. Oter, K. Ertekin, C. Kirimis, M. Koca, and M. Ahmedzade, "Characterization of a newly synthesized fluorescent benzofuran derivative and usage as a selective fiber optic sensor for Fe(III)," *Sensors and Actuators B: Chemical*. Vol. 122, 2007, pp. 450-456.
- [6] N. Malçik, and P. Çağlar, "The operational parameter of a new fibre-optic sensor for ferric ions in aqueous media," *Sensors and Actuators B: Chemical*. Vol. 38, 1997, pp. 386-389.
- [7] X. B. Zhang, G. Cheng, W. J. Zhang, G.L. Shen, and R.Q. Yu, "A fluorescent chemical sensor for Fe(III) based on blocking of intramolecular proton transfer of a quinazolinone derivative," *Talanta*. Vol. 71, 2007, pp. 171-177.
- [8] P. P. Tofiño, J. M. Barrero-Moreno and M. C. Pérez-Conde, "A flow-through fluorescent sensor to determine Fe(III) and total inorganic iron," *Talanta*. Vol. 51, 1999, pp. 537-545.
- [9] G. Ozturk, S. Alp, and K. Ertekin, "Fluorescence emission studied of 4-(2-furylmethylene)-2-phenyl-5-oxazolone embedded in polymer thin film and detection of Fe³⁺ ion," *Dyes and Pigments*. Vol. 72, 2007, pp. 150-156.
- [10] M. Zhang, B. Zheng, H. Yuan, and D. Xiao, "A spectrofluorimetric sensor based on grape skin tissue for determination of iron(III)," *Bulletin of the Chemical Society of Ethiopia*. Vol. 24(1), 2010, pp. 31-37.
- [11] A. E. Greenberg, L. S. Clesceri, and A. D. Eaton, *Standard Methods for Examination of Water and Wastewater*, 18th ed., American public health association, Washington, 1992. pp. 328-329.



K. Kajsanthia got a B. Sc. (Chemistry) in 2008 from Mahasarakham University, Thailand. She is pursuing an M. S. in Chemistry at Suranaree University of Technology, Thailand with Science Achievement Scholarship of Thailand, SAST.



J. Wittayakun is an associate professor at School of Chemistry at Suranaree University of Technology, Thailand. He got B. Sc. (Chemistry) in 1991 from Khon Kaen University, Thailand, M. S. (Chemistry) in 1995 from Colorado School of Mines, USA, and Ph. D. (Chemistry) in 2000 from University of Wisconsin-Madison, USA.



S. Prayoonpokarach is an assistant professor at School of Chemistry at Suranaree University of Technology, Thailand. He got B. Sc. (Chemistry) in 1994 from Khon Kaen University, Thailand, M. S. (Chemistry) in 2000 from Oregon State University, USA, and Ph. D. (Chemistry) in 2003 also from Oregon State University, USA.