Analytica Chimica Acta 851 (2014) 87–94

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A visual strip sensor for determination of iron

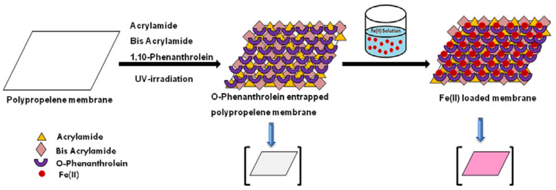
Sanjukta A. Kumar[a,*], Neha Thakur[a], Harshala J. Parab[a], Shailaja P. Pandey[a], Rakesh N. Shinde[b], Ashok K. Pandey[b], Sangita D. Kumar[a], A.V.R. Reddy[a]

[a] *Analytical Chemistry Division, BARC, Trombay, Mumbai 400085, India*
[b] *Radiochemistry Division, BARC, Trombay, Mumbai 400085, India*

HIGHLIGHTS

- A visual strip sensor for on-site detection of iron has been developed and made.
- The sensor is easy to synthesize, portable and recyclable with shelf life >1 year.
- Visual detection limit for iron using the present sensor is 50 ng mL^{-1}.
- Visual strip sensor was applied to ground water and fruit juices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form 20 August 2014
Accepted 25 August 2014
Available online 29 August 2014

Keywords:
Visual strip sensor
Iron
1,10-Phenanthroline
Acrylamide
Poly(propylene)
Ground water

ABSTRACT

A visual strip has been developed for sensing iron in different aqueous samples like natural water and fruit juices. The sensor has been synthesized by UV-radiation induced graft polymerization of acrylamide monomer in microporous poly(propylene) base. For physical immobilization of iron selective reagent, the *in situ* polymerization of acrylamide has been carried out in the presence of 1,10-phenanthroline. The loaded strip on interaction with Fe(II) in aqueous solution turned into orange red color and the intensity of the color was found to be directly proportional to the amount of Fe(II) in the aqueous sample. The minimal sensor response with naked eye was found for 50 ng mL^{-1} of Fe in 15 min of interaction. However, as low as 20 ng mL^{-1} Fe could be quantified using a spectrophotometer. The detection limit calculated using the 3*s*/*S* criteria, where ‘*s*’ is the standard deviation of the absorbance of blank reagent loaded strip and ‘*S*’ is the slope of the linear calibration plot, was 1.0 ng mL^{-1}. The strip was applied to measure Fe in a variety of samples such as ground water and fruit juices.

1. Introduction

Iron and its compounds have widespread industrial applications such as for making construction materials, drinking-water pipes, food colors, coagulants in water treatment and pigments in paints and plastics. Depending on the application and site of use varying quantities of iron are discharged into the aquatic environment. Iron is not only an essential element for the formation of hemoglobin of red cells but also vital for the storage and transport of oxygen to tissues. However, for most of the trace elements that are considered to be essential (including iron) physiologically, there exists a ‘concentration window’ for each element between the essential and toxic levels. Iron is a moderately toxic element as compared to other transition metals. Limit for iron in drinking water set by the World Health Organisation (WHO) and Bureau of Indian Standard (BIS) are 0.3 mg L^{-1} and 1.0 mg L^{-1} respectively. At low concentrations, iron plays an important role in metabolic and fermentation processes, as an enzyme activator, stabilizer and functional component of proteins. High doses of iron and its compounds can

---

* Corresponding author. Tel.: +91 22 2559 0316; fax: +91 22 2550 5329.
E-mail address: sanjuktaak301@gmail.com (S.A. Kumar).

http://dx.doi.org/10.1016/j.aca.2014.08.047
0003-2670/© 2014 Elsevier B.V. All rights reserved.

lead to serious health problems, including depression, rapid and shallow respiration, coma, convulsions and cardiac arrest [1–3]. Iron is indispensable for most of the organisms, and both its deficiency and excess could result in various disorders. In view of this, development of reliable sensing methods for iron is of considerable importance to use in environment and human health applications.

Several methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [4–7], inductively coupled plasma mass spectrometry (ICP-MS) [4,6,8] and atomic absorption spectroscopy (AAS) [8–10] are routinely used for identification and quantification of trace levels of metals in various matrices. These instrumental methods are expensive and need trained personnel to carry out the analysis of samples. On the other hand, simple and low-cost techniques like colorimetry [11,12], fluorimetry [13,14], voltammetry [15,16] and potentiometry [17,18] are also frequently used for metal ion detection and quantification. Though, many of these methods are ultrasensitive and relatively precise, they require significant time particularly when a large number of samples require testing, and are generally not amenable to on-site application by unskilled personnel.

In this context, colorimetric strip sensors have emerged as simple, inexpensive and naked eye diagnostic tools amenable for the on-site metal ion detection. There are a few reports on colorimetric strip sensors with immobilized analytical reagents or enzymes for preconcentration and quantification of various metals [19–21] and compounds [22–25]. Qi et al. have prepared Cu(II) strip sensors loaded with reagents having acylthiosemicarbazide and nitrophenyl groups [26]. This sensor showed selectivity for Cu(II) in DMSO/H_2O binary solutions. Thanyapan et al. have electrospun poly(caprolactone) and dimethylglyoxime blend into fibers, which served as an optical sensor for the nickel detection based on the formation of a red $Ni(DMG)_2$ complex [27]. Susan et al. have reported an optical strip sensor with mordant blue 29–CTAB ion pair immobilized on triacetyl cellulose membranes for the determination of UO_2^{2+} ions [28]. Literature survey revealed that fluorescent chemical sensors for Fe(III), which include molecular clips based on glycoluril [29], rhodamine [30], quinazolinone [31], benzofuran [32], 1,8-iquinolylnaphthalene [33] and boron-dipyrromethene [34] derivatives are reported. Junyan et al. developed a colorimetric sensor for Fe(III) by using a pyridyl-appended calix[4] arene and silver nanoparticles [35]. Cheng-Xiong et al. have reported a highly selective and sensitive detection method of Fe (III) in the aqueous solution by the use of MIL-53(Al) in a metal-organic frame work [36]. A Fe(III) selective fluorescent sensor based on a pyrazoline unit was used for the determination of Fe(III) ion with high selectivity in THF and in THF/water (95:5, v/v) medium by Hu et al. [37]. Vlascici et al. developed a iron(III)-potentiometric sensor based on 5-(4-carboxyphenyl)-10,15,20-tris (4-phenoxyphenyl)-porphyrin, plasticized with bis(2-ethylhexyl) sebacate [38]. An efficient and selective fluorimetric optode membrane for Fe(III) detection at low concentration levels was developed based on the quenching of the fluorescence emission of 5-(8-hydroxy-2-quinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane upon selective complexation with ferric ions [39]. All these sensors are for Fe(III). To the best of our knowledge colorimetric strip sensors for detection of Fe(II) are scanty. Jaunakais reported a test strip for detection of Fe(II) using a reagent, 2,4,6-tri (2-pyridinyl)-1,3,5-triazine (TPTZ) [40]. Till date no report is available on the use of 1,10-phenanthroline as a chromophoric reagent for preparing a strip sensor of Fe(II).

The main objective of the present work is to develop a visual strip that is simple and useful for quick on-site determination of iron content in aqueous samples. In the present work, a visual strip has been developed by immobilizing 1,10-phenanthroline in poly (acrylamide), anchored in the pores of the poly(propylene) membrane for the on-site detection of total Fe. The membrane on interaction with Fe(II) changes its color from ivory to orange red, thereby enabling the visual detection of Fe. Complete conversion of Fe(III) to Fe(II) was achieved by addition of hydroxylamine hydrochloride to the sample before adding the membrane. The applicability of the present sensor is tested for ground water and fruit juices. The possible reusability of the strip has been evaluated. The membrane is easy to use and can help a common man without the knowledge of instrumentation to visually discriminate the ground water on the basis of Fe content.

2. Experimental

2.1. Reagents and apparatus

Acrylamide (AM), *N*-*N*′-methylene-bis-acrylamide (MBA), and α,α′-dimethoxy-α-phenyl acetophenone (DMPA) were procured from Sigma–Aldrich (Steinheim, Switzerland). 1,10-phenanthroline and ferrous ammonium sulphate (for preparation of Fe(II) standard) were procured from S. D. Fine Chem. Limited, Mumbai, India. Hydroxylamine hydrochloride, methanol and *N*,*N*-dimethylformamide (DMF) were obtained from Merck (Mumbai, India). All these chemicals were used as received. Elemental iron standard ($1.0\ mg\ mL^{-1}$) from E. Merck, Germany, was used for preparing the working standards of Fe(III). Nano pure water of $18.2\ M\Omega\ cm^{-1}$ specific resistance (collected from Elix, Millipore, Merck ultra pure water system) was used throughout the experiments. Hydrochloric acid and sodium hydroxide used for adjusting the pH of solutions were of supra pure grade procured from E. Merck, Germany. The substrate used for grafting was microporous poly(propylene) flat sheet membrane (Accurel® 1E R/P from Membrana) having a pore size of 0.2 μm and thickness of 100 μm. Thickness of the membrane samples was measured using a digital micrometer (Mitutoyo, Japan) with a precision of ±0.001 mm. Multilamp photoreactor from Heber Scientific (model no. HML-SW-MW-LW-888) having six UV lamps (8 W) arranged in a circle was used for photo-initiator induced grafting. Absorbance spectra of the membranes were recorded in reflectance mode using USB 4000 spectrophotometer, Ocean Optics, Germany. Absorption spectra of the solutions were recorded using JASCO 530 UV–vis spectrophotometer, Japan. Flame atomic absorption spectrometry (FAAS) measurements were carried out using a continuum source flame atomic absorption spectrometer, Contra AA 300, Analytik Jena, Germany and graphite furnace atomic absorption spectrometer (GFAAS) measurements were carried out using Zeenith 650 GFAAS instrument of Analytik Jena, Germany.

2.2. Fabrication of the visual strip sensor

The present visual strip sensor for iron was prepared by physical entrapment of the chromophore 1,10-phenanthroline, during the *in situ* polymerization of AM, with cross-linker MBA, in the microporous poly(propylene) membrane. The polymerizing solution was prepared by dissolving monomer AM, cross-linker MBA and 1,10-phenanthroline in 3 mL DMF followed by the addition of the UV-initiator DMPA. The host poly(propylene) microporous membrane was cut into $6 \times 6\ cm^2$ size sheets and immersed in the polymerizing solution for overnight. The excess polymerizing solution adhering on the surface of the substrate was removed and the solution filled substrate was sandwiched between two transparent polyester sheets to prevent any possible loss of solution filled in the pores. Care was taken to remove excess grafting solution and, air bubbles trapped between the membrane and polyester sheets covering the membrane surface. The sandwiched substrate was exposed to UV light (365 nm) for 15 min in a multilamps photoreactor. After irradiation, the