Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 208 (2019) 40–47

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Portable and selective colorimetric film and digital image colorimetry for detection of iron

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ARTICLE INFO

Article history:
Received 18 July 2018
Received in revised form 3 September 2018
Accepted 30 September 2018
Available online 02 October 2018

Keywords:
Iron sensing
Tapioca film
Phenanthroline film
Digital image colorimetry
iPhone

ABSTRACT

Iron is an important trace element in environmental and biological systems, the development of simple and selective methods for the determination of iron is important. In this work, completely biodegradable tapioca starch was introduced as the substrate to entrap standard chromogenic probes (1,10-phenanthroline) for fabrication of a novel colorimetric sensor for ferrous. A clear plasticized thin film from tapioca starch was fabricated inside a small plastic tube as a portable test kit. A red complex was obtained by exposing the film to a ferrous solution, while no color changes were obtained with various other ions, indicating excellent selectivity. The developed films were applied in conjunction with a digital image colorimetry for quantification of ferrous. Calculated molecular absorption of the red complex showed the widest linear range (0 to 10 mg L^{-1}) with good linearity (R^2 < 0.9934) with ferrous concentrations. The developed method provided good inter-day precision (1.75 to 3.97% RSD, 5 days 15 sensors), good accuracy (+2.35% to +4.57% relative error), and low detection limit (0.09 ± 0.01 mg L^{-1}). The concentrations of ferrous ion in soil and water samples quantified by the developed method were not significantly different from atomic absorption spectrophotometry at 95% confidence level. The films were stable for at least three months.

1. Introduction

Iron (Fe) is an important trace element in environmental and biological systems. Although iron is a naturally occurring element, commonly present in rock and soil, large concentrations of reduced iron (Fe^{2+}) in solution may be toxic to plants [1]. Iron is also an essential transition metal involved in various human metabolic pathways, *e.g.* the oxygen-transport mechanism and acting as a cofactor. Iron deficiency may cause loss of motor skills [2], while deposition of it in the central nervous system is involved in a number of diseases [3,4]. Ferrous iron also causes the formation of hydroxyl radicals [5], contributing to lipid peroxidation [6], and DNA damage [7]. Therefore, the development of simple and selective methods for the determination of iron has received particular attention.

Recently, a number of chemosensors have been developed for the detection of iron [8–20] to overcome the disadvantages of conventional instrumental methods, such as cumbersome and expensive optical equipment, complicated operating procedures, and tedious pretreatment of samples. Various selective reagents have been reported for the detection of ferric ions, *e.g.* curcumin [15], D-penicillamine-functionalized graphene quantum dots [19], alcohol-soluble poly(9-fluorenecarboxylic acid) [20], triazole [17], rhodamine G [21]; as well as for ferrous ions, *e.g.* phenanthroline and bathophenanthroline [12,22], 2-(2′-pyridyl)imidazole [13], ferrozine [22], and ferene S [22]. These selective reagents may be trapped within filter paper to fabricate selective test strips [23], while polymer materials have also been reported as substrates to entrap and avoid leakage of these selective reagents, *e.g.* electrospun nanofiber [13], and hydrogel [12,21]. These materials, *e.g.* poly-vinylbenzene chloride used to fabricate nanofiber [13], are synthetic polymers and may be toxic to the environment due to resisting degradation. The organic solvents commonly used to dissolve such materials, *e.g.* dimethylformamide and tetrahydrofuran [13], are also toxic. The use of biodegradable natural polymers as substrate in fabrication of selective iron sensors could overcome this drawback.

Recently, natural polymers have been receiving growing attention due to their inherent biodegradability [24]. Starch is the most abundant polysaccharide in plants, and is composed of two homopolymers of D-glucose, amylose and amylopectin [24–26]. Due to its film-forming properties and other advantages that include low cost and wide availability, starch has been widely used to fabricate renewable and biodegradable films for various applications [24,27]. The ratio of amylose and amylopectin influences mechanical properties of the starch films,

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https://doi.org/10.1016/j.saa.2018.09.062
1386-1425/

and amylose is preferable for good film properties [28]. Due to hydrophilic nature and brittleness of starch films, plasticizers such as glycerol may be used [29–31].

In this work, natural biodegradable polymers were used for the first time as the substrate to fabricate environmentally friendly colorimetric films for the detection of ferrous ions. The ferrous-selective reagent, 1,10-phenanthroline (phen), was entrapped within biodegradable films from tapioca starch. The films were then used in conjunction with digital image analysis, instead of conventional spectrophotometric measurement, to facilitate on-site detection. Digital image technology is increasingly used in the quantification of analytes [32–40]. It is based on analysis of the basic red/green/blue (RGB) color layers in a digital image of the colorimetric product. The RGB data were calibrated for the quantification of analytes. In this work, the on-site quantification of ferrous ions employed a common smartphone, which is more convenient and cost effective than a spectrophotometer.

2. Materials and Methods

2.1. Materials

Ferrous (II) sulfate heptahydrate was purchased from Merck (Darmstadt, Germany). Tapioca starch was purchased from a supermarket in Kathu, Phuket, while glycerol was obtained from Ajax FinechemPty Ltd. 1,10-Phenanthroline monohydrate was purchased from Fisher scientific UK Limited (Leicestershire, UK). Ultrapure water (type I) was obtained from Merck water purification system (Elix Essential 5).

2.2. Preparation of the Phenanthroline-based Tapioca Starch Colorimetric Films (Phen-film)

The phen-films were prepared by entrapment of phen within thin films of tapioca starch. Tapioca starch (0.5 g) was dispersed in ultrapure water (10 mL) before heating on a hotplate (~120 °C) under continuous stirring until a clear viscous solution was obtained. Glycerol (0.10 mL) was added with stirring for 3–4 min to obtain a homogenous solution. After the resultant solution was cooled to room temperature, phen (0.1 g) was added and stirred for 4–5 min. One hundred microliters of the mixture was then transferred into a 1.5 mL plastic tube and vertically incubated at 100 °C for 90 min in an oven. After the tube was cooled to room temperature it was quickly closed to avoid any contamination before storage in a refrigerator prior to further use.

2.3. Preparation of the Acidic Tapioca Starch Thin Films (Acidic-film) for Sample Preparation

As acidic conditions are required in sample preparation for ferrous detection, acidic-films were prepared to facilitate on-site use. The acidic-film was prepared using similar preparation procedure as for the colorimetric thin films (Section 2.2). Hydrochloric acid (5 mL, 6 M) was used instead of the colorimetric reagent. The mixture

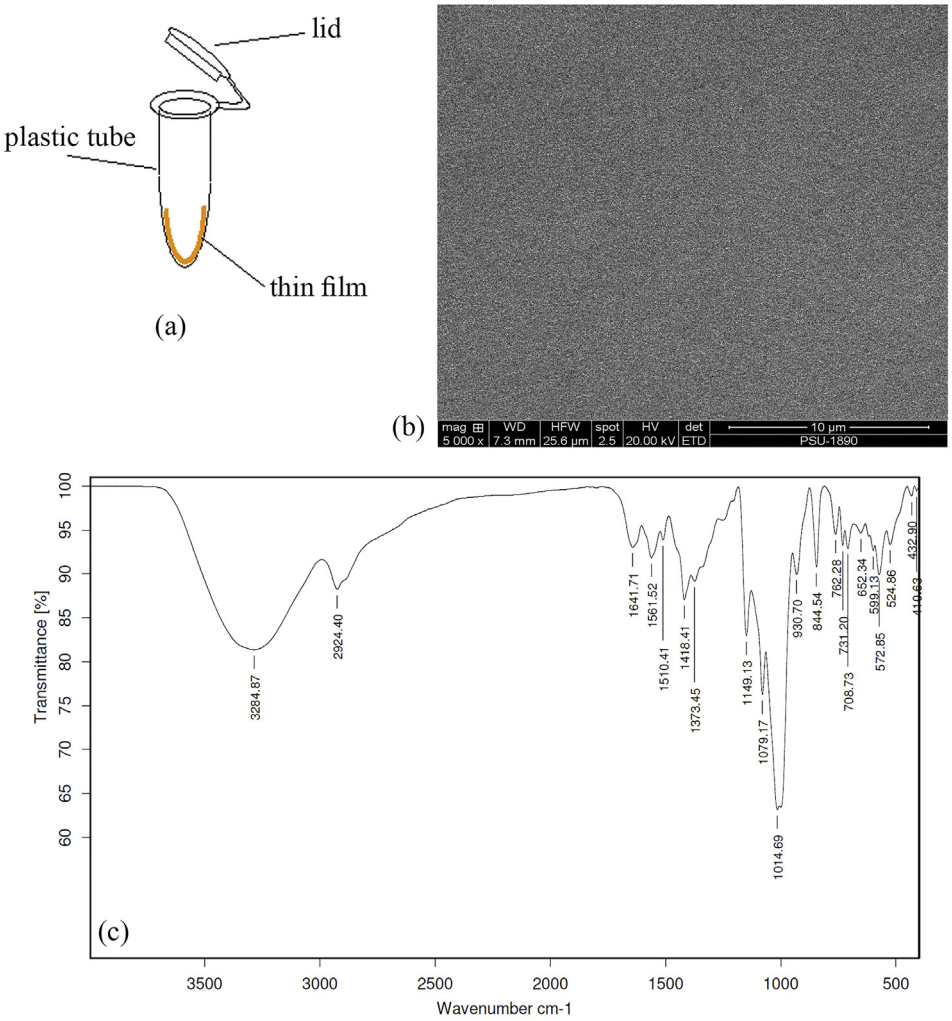

Fig. 1. (a) The phen-film cast in a small plastic tube, (b) SEM images, and (c) FTIR spectrum of the phen-film.