Food Chemistry 230 (2017) 667–672

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Dispersive liquid-liquid microextraction coupled with digital image colorimetric analysis for detection of total iron in water and food samples

Bo Peng [a,*], Guorong Chen [a], Kai Li [a], Min Zhou [a], Ji Zhang [b], Shengguo Zhao [c]

[a] Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China
[b] College of Life Science, Northwest Normal University, Lanzhou 730070, China
[c] Gansu Entry-Exit Inspection and Quarantine Bureau, Lanzhou 730020, China

ARTICLE INFO

Article history:
Received 18 October 2016
Received in revised form 12 March 2017
Accepted 17 March 2017
Available online 18 March 2017

Keywords:
Iron
Microextraction
ImageJ
Colorimetric
Scanner

ABSTRACT

A simple and low cost assay for total iron in various samples based on dispersive liquid-liquid microextraction (DLLME) coupled with digital scanning image analysis was proposed. Orthogonal experiment design was utilized to optimize the amount of extraction solvent and disperser solvent, O-phenanthroline concentration and buffer pH. Under the optimum conditions, the calibration curve was linear over the range of 0.047–1.0 μg mL^{-1} ($R^2 > 0.99$) of iron. The limit of detection (LOD) for iron was 14.1 μg L^{-1} and limit of quantification (LOQ) was 46.5 μg L^{-1}. The relative standard deviations for seven replicate determinations of 0.5 μg mL^{-1} of iron was 3.75%. The method was successfully applied for analysis of total iron in water and food samples without using any spectral instrument and it could have a potential industrial impact in developing fast and portable devices to analyze the iron content in water and certain foods.

1. Introduction

Iron is the most abundant prominent element in nature and it is one of the most important elements in environmental and biological. Conventional laboratory-based iron detection methods include atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), UV–Vis spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis, etc. These methods require several time consuming manipulation steps, bulky and expensive equipment for measurement sensitivity and accuracy, while there are still many cases when on-site is preferred such as point-of-care. Computer vision-based analytical procedure (Capitan-Vallvey, Lopez-Ruiz, Martinez-Olmos, Erenas, & Palma, 2015) related to digital image colorimetric analysis (Costa et al., 2015) is becoming powerful, fast and low-cost tools, especially in resource-limited settings. Computer vision-based assays are good at low cost and executable at remote sites with visual assessment of color changes, which correlate with analyte concentration.

The analytical use of color-based methods is very diverse and has increased in the last decade (Lapresta-Fernández & Capitán-Vallvey, 2011). A desktop scanner with digital imaging can be used to determine the concentration of a starch-iodine complex, food coloring solutions (Kohl, Landmark, & Stickle, 2006; Mathews, Landmark, & Stickle, 2004), nitrogen dioxide in air (Passaretti Filho, da Silveira Petruci, & Cardoso, 2015), phosphorus in water (Chuanxiao Yang, Liu, & Lian, 2007; Meng, Schultz, Cui, Li, & Yu, 2015). The digital imaging analysis of a scanned microplate image can also be performed accurately and inexpensively for popular teaching and learning activities such as water-quality monitoring (Soldat, Barak, & Lepore, 2009). Using those consumer electronics devices, such as mobile phones or flatbed scanners for biomedical imaging and sensing has several advantages over traditional microscopy approaches (Christodouleas, Nemiroski, Kumar, & Whitesides, 2015; Gorocs & Ozcan, 2014). The normal mode of these methods is characterized in that the colored sample solution was took a digital picture by ordinary household imaging devices. The integration value of photos was read by image processing software and the quantitative relationship between color space value and concentration can be established. A multivariate calibration method based on RGB color space (Red, green and blue, respectively), HSI color space (Hue, saturation and intensity, respectively)

* Corresponding author.
E-mail address: pengbo.nwnu@hotmail.com (B. Peng).

http://dx.doi.org/10.1016/j.foodchem.2017.03.099
0308-8146/

and gray intensity histograms was developed and validated (de Lelis Medeiros de Morais & Gomes de Lima, 2015). Many substances, such as the glucose, creatinine, triglycerides, total cholesterol, total protein, nitrite, potassium and inorganic arsenic in blood samples (de Morais & de Lima, 2014), unset yellow (Botelho, de Assis, & Sena, 2014), horseradish peroxidase (Parween & Nahar, 2015), organophosphorus pesticides in food products (Meng et al., 2015), tetracycline in milk (Masawat, Harfield, & Namwong, 2015), serum samples (de Lelis Medeiros de Morais & Gomes de Lima, 2015), saliva samples (Thiago, Cardoso, & Coltro, 2015), beverages (Lapresta-Fernández & Capitán-Vallvey, 2011) and drinking water (Kearns & Tyson, 2012) were efficiently analyzed. The digital image analysis of a scanned microplate image could be a potential alternative for a spectrophotometer dealing with quantitative microscale procedures (Soldat et al., 2009) and enable the development of methods for micro-flow batch analyses (Gorocs & Ozcan, 2014) and for point-of-care (POC) diagnostics (Christodouleas et al., 2015).

As a powerful pre-enrichment method, the dispersive liquid-liquid microextraction (DLLME) (Rezaee et al., 2006) possess obvious advantages of simple operation with a high enrichment factor, low-cost, and low consumption of organic solvent (Ojeda & Rojas, 2009; Rezaee, Yamini, & Faraji, 2010) for separation and enrichment of the target. Therefore, DLLME can reasonably improve the level of sensitivity in many analytical procedures with a minimum sampling volume. Trace vanadium (Zongqing Ding & Liu, 2009), copper (Ying Yuan & Lv, 2013) in water and nitrite (Ding & Liu, 2009) in environmental and biological samples were successfully determined by using digital scan image analysis coupled with DLLME.

Here, we report the development a method of DLLME coupled with digital image profiling for determination of total iron. The extractable orange-red ion-association complex of Fe (II)-o-phenanthroline with picrate was first enriched by DLLME. Then the extracted organic phase was spotted onto a TLC plate and directly scanned. Different flatbed scanner systems have been employed in the TLC-quantitative evaluation of various classes of compounds (Cobzac, Casoni, Fazaka Lucian, & Sârbu, 2012; Sima, Casoni, & Sârbu, 2013). The image was processed and analyzed with a public domain Java-based image processing program ImageJ (Schneider, Rasband, & Eliceiri, 2012), which enables us to calculate color intensities in a tablet or notebook. The intensity of grey-scale spot is represented as Integrated Optical Density (IOD) (Asahara et al., 1998; Kayser, Liewald, Kremer, & Tacke, 1994) which is readily measured through Gel Analysis method of ImageJ (Vaher & Kaljurand, 2012; Vaher et al., 2014). The linear relationship between the intensity of sample spot obtained from ImageJ and iron concentration was established for quantitative determination (Hartig, 2013; Miller, 2007, November 04, 2010). The proposed method combines the advantages of DLLME and the convenience of computer processing of images analysis. Our work is aimed to explorer a simple, low cost and potentially portable detection method for analyte related to conventional colorimetry system without using any large-scale spectral instrument.

2. Experimental

2.1. Apparatus

An Acer scanner (Scanprisa 640U) with the silia gel TLC plate (G) was used for digital scanning colorimetric method. A flame atomic absorption spectrometer (AAS) (Hitachi Z-2000) was utilized, equipped with a 100 mm burner head, Zeeman background correction and an air–acetylene flame. An iron hollow-cathode lamp (General Research Institute for Nonferrous Metals, Beijing) was used as radiation source, operated at 7 mA with a slit width of 0.2 nm. The wavelength for iron detection was set at 248.3 nm resonance line. The acetylene and the air-flow rates were 1.8 and 10.0 L min^{-1}, respectively. The digested samples were filtered through the ultra filtration membrane with pore size of 4 nm before analyzed. A centrifuge (80-1) with 15 mL calibrated centrifuge tube for accelerating the process of the phase separation. A pH-meter (PHS-3C) was used to measure pH values. An oscillator (HY-4/KS-1) was used to promote the reaction. An electric hotplate was used for heating in the process of samples digestion.

2.2. Reagents

Stock standard solution of Fe (III) at a concentration of 1000 μg mL^{-1} in 1.0 mol L^{-1} HNO_3 was purchased from National Non-ferrous Metal & Electronic Material Analytical and Testing Center (Beijing, China). Working solution of Fe (III) was prepared by appropriate step-by-step dilution of the stock standard solution. O-phenanthroline and picric acid solution were purchased from Taishan chemical industry Co., Ltd. (Guangdong, China). Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), ethanol, NaOH and HCl were obtained from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Acetic acid and sodium acetate were provided by Tianjin Kaitong Chemical Reagent Co., Ltd. (Tianjin, China). The water certified reference materials (GSBZ50019-90, GBW (E) 080195) purchased from National Research Center for Certified Reference Materials (Beijing, China) and GBW08616 (National Non-ferrous Metal & Electronic Material Analytical and Testing Center, Beijing, China) were used for validation of the proposed method. A 10% (m/v) solution of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was prepared by dissolving appropriate amount of NH_2OH-HCl in deionized water. A 0.05 mol L^{-1} picric acid solution was prepared by dissolving appropriate amount of picric acid in 5.0 mL of ethanol and 2.0 mL of 1.0 mol L^{-1} NaOH solution and diluting to 50 mL in deionized water. A 0.5 g L^{-1} O-phenanthroline solution was prepared by dissolving appropriate amount of this reagent and diluting to 100 mL in deionized water. A 1.0 mol L^{-1} acetic acid-sodium acetate buffer solutions (pH = 3.0–8.0) were prepared from 1.0 mol L^{-1} acetic acid and 1.0 mol L^{-1} sodium acetate, while 1.0 mol L^{-1} HCl was used to adjust pH below 3.0 and 1.0 mol L^{-1} NaOH was used to adjust pH over 7.0. All reagents used in this work were of analytical reagent grade unless otherwise stated. Ultra pure water was used throughout the work.

2.3. Procedure for DLLME

In the experiment, 0.5 mL working solution of Fe (III) was placed into a 15 mL centrifuge tubes and mixed with 0.2 mL 10% hydroxylamine hydrochloride solution. After Fe (III) ions are completely reduced, the solution containing 1.0 mL of 0.5 g L^{-1} O-phenanthroline and 1.5 mL acetic acid-sodium acetate buffer solution (pH = 5.5) were added and diluted to 10.0 mL. Then, 0.5 mL 0.05 mol L^{-1} picric acid solution was added. The contents were mixed well and the tubes left to stand for 1 min. Then, a mixture of 1000 μL methanol (as disperser solvent) and 140 μL chloroform (as extraction solvent) was injected into the sample solution by using a syringe rapidly. After the injection and shaking for 3 min, a cloudy mixture was formed. The tube was centrifuged for 5 min at 3500 rpm. The bulk aqueous phase was removed by a syringe, while extracted organic phase 3 μL was dropped onto the TLC plate. The colored spots at different intensity were developed. The color intensity on the TLC plate can remain constant at least four hours.