Talanta 137 (2015) 25–30

Contents lists available at ScienceDirect

Talanta

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

Redox speciation analysis of dissolved iron in estuarine and coastal waters with on-line solid phase extraction and graphite furnace atomic absorption spectrometry detection

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ARTICLE INFO

Article history:
Received 26 September 2014
Received in revised form
5 January 2015
Accepted 10 January 2015
Available online 20 January 2015

Keywords:
Dissolved iron redox speciation
Flow injection analysis
Solid phase extraction
Estuarine and coastal waters
Graphite furnace atomic absorption spectrometry

ABSTRACT

An automatic on-line solid phase extraction (SPE) system employing the flow injection (FI) technique directly coupled to a graphite furnace atomic absorption spectrometer (GFAAS) was established for speciation and determination of dissolved iron in estuarine and coastal waters. Fe(II) was mixed with ferrozine solution in a sample stream to form the Fe(II)–ferrozine complex which was extracted onto a C18 SPE cartridge, eluted with eluent and detected with GFAAS. In a parallel flow channel, Fe(III) was reduced to Fe(II) with ascorbic acid and then detected in the same way as Fe(II). The home-made interface between FI–SPE and GFAAS efficiently realized the sample introduction to the furnace in a semi-automated way. Parameters of the FI–SPE system and graphite furnace program were optimized based on a univariate experimental design and an orthogonal array design. The salinity effect on the method sensitivity was investigated. The proposed method provided a detection limit of 1.38 nmol L^{-1} for Fe(II) and 1.87 nmol L^{-1} for Fe(II+III). With variation of the sample loading volume, a broadened determination range of 2.5–200 nmol L^{-1} iron could be obtained. The proposed method was successfully applied to analyze iron species in samples collected from the Jiulongjiang Estuary, Fujian, China. With the 2-cartridge FI–SPE system developed, on-line simultaneous determination of Fe species with GFAAS was achieved for the first time.

1. Introduction

At very low concentrations (typically <1 nmol L^{-1}) in ocean waters [1], iron has attracted considerable attention in the recent 25 years. It controls the growth of phytoplankton in high-nutrient, low-chlorophyll areas consisting of more than 30% of the open oceans and certain coastal regions [2]. Iron is introduced into estuarine and coastal waters by riverine input, sediment resuspension and weathering of iron-containing minerals. Meanwhile, chemical processes, salt-induced flocculation and precipitation, and biological consumption scavenge iron from them [3,4]. These factors comprehensively lead to a pronounced iron concentration gradient, from the nmol L^{-1} to μmol L^{-1} level, at the land–sea margin [3,5]. Dissolved iron (traditionally defined as <0.45 or <0.2 μm filterable iron) exists in two common oxidation states, Fe(II) and Fe(III), in aqueous environments. Fe(II) has high bioavailability, and acts as an intermediate in iron uptake in the aquatic system [6–8]. It is generated at significant levels in coastal surface waters via photoreduction and bioreduction of Fe(III) with dissolved organic complexes [6,9]. Therefore, characterization of dissolved iron with differentiated redox species is important for investigating the iron biogeochemistry in estuaries and coastal areas.

Several approaches have been developed and applied to iron speciation analysis, including the flow injection (FI) technique with chemiluminescence detection [10], cathodic stripping voltammetry [11] and spectrophotometry [5,12–15]. Two commonly used spectrophotometric methods are both based on the FI technique. One utilizes the catalytic action of Fe(III) on the oxidation of *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride by hydrogen peroxide [5,12], while the other one employs the colorimetric reagent ferrozine (FZ, 3-(2-pyridyl)-5,6-diphenyl-l,2,4-triazine-*p*,*p*'-disulfonic acid) to isolate Fe(II) [14,15]. FZ has been widely applied for iron analysis owing to its high selectivity and sensitivity for Fe(II) determination. Published works prove that Fe(III) has no detectable interference to the reaction of Fe(II) and FZ, even in the sample with high Fe(III) additions [13]. FZ has been immobilized on the C18 cartridge for determination of Fe(II) and reduced Fe(III) in seawater owing to its specific formation of the stable Fe(II)–FZ complex [13,14]. The immobilized C18 cartridge is used to remove the major matrix as well as to quantitatively retain

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http://dx.doi.org/10.1016/j.talanta.2015.01.017
0039-9140/

the Fe(II) as the Fe(II)–FZ complex when the seawater sample is applied. The complex can be eluted with methanol, and then measured spectrophotometrically. However, the excess FZ can cause a detection error when iron at relatively low concentration is present in the eluate [16]. Additionally, Cu(I), Co(II) and Ni(II) can form colored FZ complex and contribute a significant interference in Fe(II) spectrophotometric determination [13].

Compared with spectrophotometry, graphite furnace atomic absorption spectrometry (GFAAS) is a superior option for trace iron determination due to its high selectivity. It is a robust analytical technique with high sensitivity, low limits of detection and low consumption of sample [17]. Especially for iron with AAS determination, the mentioned metal interference is eliminated. However, the organic material and high salinity matrix can intensify background interference on absorbance measurements despite the use of background correction devices. Therefore, separation and preconcentration of iron from seawater is necessary. Successful methods of matrix separation mainly include precipitation and coprecipitation, solvent extraction, and solid phase extraction (SPE), both off-line and on-line. The implementation of an on-line sample processing system plays an important role in the transfer of analyte to GFAAS. Even though the discrete sample presentation of GFAAS limits the on-line coupling system, the continuously flowing system with the SPE technique has been hyphenated with GFAAS [18,19].

The symbiosis of the FI–SPE separation and preconcentration system and GFAAS has proved feasible, although still troublesome, for the determination of trace metals in seawater [18,19]. In the developed on-line coupled systems, SPE columns are packed with silica-immobilized 8-hydroxyquinoline [20] or Chelex-100 resin [21] for determination of total dissolved iron or Fe(III) only. In a recent study, speciation of Fe(II) and Fe(III) in atmospheric water utilizing the FZ method and off-line GFAAS analysis is reported [22]. Fe(II) is retained on a FZ conditioned cartridge and eluted with a water–methanol solution. Unretained Fe(III) is directly collected at the outlet of the cartridge. Thus, Fe(II) and Fe(III) are separated and further determined with GFAAS.

It is recognized that the GFAAS technique coupled with FI for iron analysis is lack of an efficient interface for on-line speciation and detection. Nevertheless, the previous works on an iron speciation method and development of interface between FI and GFAAS have enlightened on the design of a connected parallel system for automatic FI–SPE preconcentration procedure and graphite furnace operation.

Based on the reaction of FZ and Fe(II), a method for the simultaneous determination of Fe(II) and total dissolved iron (named Fe (II+III) here) in estuarine and coastal waters was developed in this study, using an automatic FI–SPE system hyphenated with GFAAS. The Fe(III) concentration was calculated by subtracting Fe(II) concentration from Fe(II+III). The key point of the system, interface of the FI system and GFAAS, was established. A 10-port valve installed with a pair of C18 cartridges was employed for the alternate and successive separation of Fe(II) and Fe(II+III). The iron–FZ complex formed in the FI–SPE system was transferred via the interface to GFAAS for detection. The graphite furnace thermal program was optimized to accommodate the analysis of the organic iron complex in the matrix of a high level of organic materials, of ethanol, and FZ. The proposed method was successfully applied to analyze natural waters collected from the Jiulongjiang Estuary, Fujian, China.

2. Experimental

2.1. Reagents and standards

Ultrapure water (UP, $>18\ M\Omega\ cm$) obtained from a Milli-Q water purification system (Millipore, USA) was used for the preparation of all solutions. Reagents and standards were prepared in a clean air flow hood to eliminate contamination. Plastic bottles for storing reagent solutions, standards and seawater samples were low/high-density polyethylene (LDPE/HDPE, Nalgene, USA) bottles, washed following the accepted protocol [8] and sealed in double plastic bags. Two small holes were drilled in the cap of each bottle, one as the solution outlet and the other one equipped with a 0.22 μm pore size filter as a particle-free air inlet [5]. Thus, contamination of the solutions in use could be prevented even if no clean bench was provided.

All HCl solutions were prepared by diluting certain amounts of 30% (v/v) HCl (Suprapur®, Merck, Germany) in UP water. Fe(II) stock standard solution (0.01 mol L^{-1}) was prepared monthly and obtained by dissolving 0.3921 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (puriss p. a., 99.0%, Fluka®, Sigma-Aldrich, USA) in 100 mL 0.1 mol L^{-1} HCl solution. Fe(III) stock solution was the commercial iron atomic absorption standards (1000 mg L^{-1}, CertiPUR®, Merck, Germany). Low iron seawater (LISW, salinity approximately 35) was collected from the surface of the South China Sea using a towed fish underway sampling system, filtered through a 0.2 μm membrane filter (Millipore, USA) and acidified to pH 1.7. Fe(II) and Fe(III) working solutions were prepared daily by appropriate dilutions in 0.01 mol L^{-1} HCl or acidified LISW.

Ferrozine ($C_{20}H_{13}N_4NaO_6S_2$, ≥97.0%, Sigma-Aldrich, USA) of 0.4925 g was dissolved in 100 mL UP water to prepare the 0.01 mol L^{-1} FZ stock solution. The 2.5 mol L^{-1} ammonium acetate buffer stock solution (pH ~ 5.5) was obtained by adding 78 mL 25% (v/v) ammonia solution (Suprapur®, Merck, Germany) to 57 mL glacial acetic acid (Suprapur®, Merck, Germany), then adjusting the pH with 6 mol L^{-1} HCl solution and making up to 200 mL with UP water. The FZ and buffer stock solutions were added to UP water to prepare the FZ working solution with final concentrations of FZ 750 μmol L^{-1} and buffer 0.125 mol L^{-1}. This working solution was named FZ-II. Ascorbic acid was used as the reducing agent for Fe(III) reduction [14]. The 0.01 mol L^{-1} ascorbic acid stock solution was prepared weekly by dissolving ascorbic acid (A.R., Sinopharm Co., China) in UP water and storing it in the dark at 4 °C. For determination of Fe(II+III), the working solution was prepared daily by adding 0.5 mL ascorbic acid stock solution to 200 mL FZ-II, and was named FZ-III.

Supelclean™ LC-18 SPE cartridges (100 mg/1 mL, Supelco®, Sigma-Aldrich, USA) were modified as on-line SPE columns. The eluent for SPE contained 30% (v/v) ethanol (A.R., Sinopharm Co., China) and 0.3 mol L^{-1} HNO_3 (MESURE®, Merck, Germany). 50% (v/v) ethanol was used to condition the C18 cartridges. The rinsing solutions included UP water and 0.15 mol L^{-1} HCl. The 0.01 mol L^{-1} HCl was prepared as the pre-eluting solution.

Magnesium matrix modifier (for graphite furnace AAS, Fluka®, Sigma-Aldrich, USA) was diluted to 1:210 (v/v) with 0.07 mol L^{-1} HNO_3 to satisfy GFAAS analysis. A magnesium solution of 5 μL was needed for each sample, as recommended in the operation manual. Argon gas of ≥L was9% purity was obtained from Xinhang Industrial Gases Co., Ltd. China.

2.2. Instrumentation

The schematic diagram of the whole system is presented in Fig. 1, and could be divided into three parts, namely FI–SPE, GFAAS and the interface between them.

The FI–SPE system was constructed using a BT100-1L 4-channel peristaltic pump (P1) and a BT100-2J 2-channel peristaltic pump (P2) from Baoding Longer Precision Pump Co., China, furnished with silicone tubing as pump tubing. An 8-position selector valve (V1, VICI, Valco Instruments Co., USA) was adopted to shift the solution channels. A 10-port, 2-position injection valve (V2, VICI, Valco Instruments Co., USA) equipped with a pair of modified C18 cartridges (C) was used to select the preconcentration or elution