Cloud point extraction and graphite furnace atomic absorption spectrometry determination of manganese(II) and iron(III) in water samples

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Abstract

Cloud point extraction (CPE) was applied as a preconcentration step prior to graphite furnace atomic absorption spectrometry (GFAAS) determination of manganese(II) and iron(III) in water samples. After complexation with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), the analytes could be quantitatively extracted to the phase rich in the surfactant *p*-octylpolyethyleneglycolphenylether (Triton X-100) and be concentrated, then determined by GFAAS. The parameters affecting the extraction efficiency, such as solution pH, concentration of PMBP and Triton X-100, equilibration temperature and time, were investigated in detail. Under the optimum conditions, preconcentration of 10 ml of sample solution permitted the detection of 0.02 ng ml^{-1} of Mn(II) and 0.08 ng ml^{-1} of Fe(III) with enrichment factors of 31 and 25 for Mn(II) and Fe(III), respectively. The proposed method was applied to determination of trace manganese(II) and iron(III) in water samples with satisfactory results.
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Keywords: Cloud point extraction; Graphite furnace atomic absorption spectrometry; Manganese(II); Iron(III)

1. Introduction

Manganese is a necessity for the proper function of several enzymes and an essential micro-nutrient for the function of the brain, nervous system, and normal bone growth. It optimizes enzyme and membrane transport functions [1,2]. Iron is important in the biosphere, serving active center of a wide range of proteins, such as oxidases, reductases, and dehydrases. It plays an essential role in phytosynthesis and is a limiting growth nutrient for phytoplanktons in some parts of the open oceans [3,4]. The consumption of manganese and iron-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling, and disposal. The determination of trace amounts of manganese and iron in biological and environmental samples is important in the fields of environmental analysis, process control, and medicine [5,6].

The determination of trace manganese and iron in biological and environmental samples is difficult due to various factors, particularly low concentration and matrix effects. Although

graphite furnace atomic absorption spectrometric (GFAAS) method is a powerful analytical tool for determining trace elements in environmental samples, preconcentration and separation techniques are still necessary. The widely used techniques for the separation and preconcentration of manganese and iron include liquid–liquid extraction [7,8], coprecipitation [9,10], solid-phase extraction [11–14], etc.

Separation and preconcentration based on cloud point extraction (CPE) are becoming an important and practical application of surfactants in analytical chemistry [15,16]. The technique is based on the property of most nonionic surfactants in aqueous solutions to form micelles and to separate into a surfactant-rich phase of a small volume and a diluted aqueous phase when heated to a temperature known as the cloud point temperature. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, speedy, and of lower toxicity to the environment than those extractions that use organic solvents. Cloud point methodology has been used to separate and preconcentrate organic compounds as a step prior to their determination in hydrodynamic analytical systems such as liquid chromatography [17] and capillary electrophoresis [18]. The phase separation phenomenon has been also used

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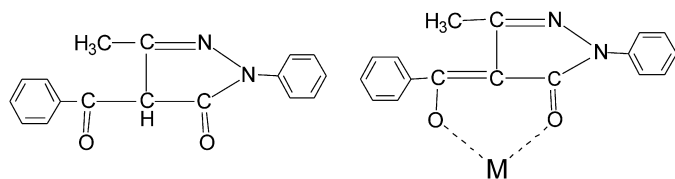*E-mail address:* liangpei@mail.ccnu.edu.cn (P. Liang).

Fig. 1. Structural formulae of PMBP and the complexe.

for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes [19,20]. CPE as a preconcentration step in conjunction with spectrophotometry, FIA-spectrofluorimetry, FAAS, ETAAS, ICP-AES, and HPLC for the determination of various metal ions has been widely studied [21–28]. CPE combination with FAAS for determination of manganese and iron has also been reported [29–34].

CPE coupled with GFAAS can attain detection limits that are up to 100 times lower compared with respective FAAS configuration [19]. In this paper, a CPE method based on the complex of Mn(II) and Fe(III) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP, its structure is shown in Fig. 1), which forms complexes with more than 40 metal ions and has found numerous applications in trace element separation and preconcentration by solvent extraction [35,36] and solid phase extraction [37,38], and using *p*-octylpolyethyleneglycolphenylether (Triton X-100) as surfactant is proposed for the preconcentration of Mn(II) and Fe(III) in water samples prior to their determination by GFAAS. The main factors affecting the cloud point extraction were evaluated and optimized. The proposed method was applied to determination of trace manganese(II) and iron(III) in water samples with satisfactory results.

2. Experimental

2.1. Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, PR China) with a deuterium background correction and a GF990 graphite furnace atomizer system was used. All measurements were performed using integrated absorbance (peak area). Hollow-cathode lamps for Mn and Fe were operated at 2 and 4 mA. The optimum operating parameters for GFAAS are given in Table 1. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, PR China) supplied with a combined electrode. A thermostated bath maintained at the desired temperatures was used for the cloud point experiments. An 80-2 centrifuge (Changzhou Guohua Electric Appliance Co. Ltd., PR China) was used to accelerate the phase separation.

2.2. Reagents and solutions

The nonionic surfactant Triton X-100 was obtained from Amresco and was used without further purification. Stock standard solution of Mn(II) and Fe(III) at a concentration of $1000\ \mu g\ ml^{-1}$ was obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A 1.2×10^{-2} M solution of PMBP was prepared by dissolving appropriate amounts of this reagent in absolute ethanol from the commercially available product (The First Reagent Factory, Shanghai, PR China). The following buffers were used to control the pH of the solutions: hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), ammonium acetate–ammonia (pH 6–8), and ammonium chloride–ammonia (pH 8–9). All other reagents were of analytical reagent grade or better. Doubly distilled water was used throughout the entire study. The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with doubly distilled water.

2.3. Procedures

For the CPE, aliquots of 10 ml of a solution containing the analytes, $2.0\ g\,L^{-1}$ Triton X-100 and 1.0×10^{-3} M PMBP buffered at a suitable pH were kept in the thermostatic bath maintained at 80 °C for 25 min. Since the surfactant density is $1.07\ g\,ml^{-1}$ therefore, the surfactant-rich phase can settle through the aqueous phase. The phase separation was accelerated by centrifuging for 5 min at 3000 rpm. After cooling in an ice-bath, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The aqueous phases can readily be discarded simply by inverting the tube. To decrease the viscosity of the extract and allow its pipetting, 200 μl of 0.1 M HNO₃ was added to the surfactant-rich phase. 20 μl sample was introduced into the GFAAS by manual injection. Calibra-

Table 1
Operating parameters for GFAAS

Parameters	Mn	Fe
Lamp current (mA)	2.0	4.0
Wavelength (nm)	279.5	249.3
Slit (nm)		0.2
Ar flow rate (ml min⁻¹)		200 (stopped during atomizing)
Sample volume (μl)		20
Temperature program		
Drying	100 °C (Ramp 20s, Hold 10s)	120 °C (Ramp 20s, Hold 10s)
Ashing	600 °C (Ramp 10s, Hold 18s)	1000 °C (Ramp 10s, Hold 20s)
Atomizing	2400 °C (Ramp 0s, Hold 3s)	2100 °C (Ramp 0s, Hold 3s)
Cleaning	2600 °C (Ramp 1s, Hold 3s)	2400 °C (Ramp 1s, Hold 3s)