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Solid phase preconcentration of iron as methylthymol blue complex on naphthalene-tetraoctylammonium bromide adsorbent with subsequent flame atomic absorption determination

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Abstract

A sensitive and selective preconcentration method for the determination of trace amounts of iron by atomic absorption spectrometry has been developed. Iron forms a complex with methylthymol blue at $\mathrm{pH} = 3$. This complex is retained by naphthalene tetraoctylammonium bromide adsorbent in a column with a height of about 2 cm. The adsorbed metal complex is then eluted from the column with nitric acid and its iron content is determined by flame atomic absorption spectrometry (FAAS). The effect of different variables such as pH, reagent concentration, flow rate and interfering ions on the recovery of the analyte was investigated. The calibration graph was linear in the range 25–350 $\mathrm{ng\,ml^{-1}}$ of iron in the initial solution with $r = 0.9994$. The limit of detection based on $3S_\mathrm{b}$ criterion was 12 $\mathrm{ng\,ml^{-1}}$ and the relative standard deviation for eight replicate measurements of 150 and 300 $\mathrm{ng\,ml^{-1}}$ of iron was 3.1 and 1.8%, respectively. This procedure was successfully applied to the determination of iron in tap and sewage water samples.

Keywords: Iron; Preconcentration; Methylthymol blue; Atomic absorption spectrometric; Naphthalene-tetraoctylammonium bromide adsorbent

1. Introduction

It is important to determine trace amounts of iron in water for environmental protection, hydrogeology and some chemical processes [1]. Flame atomic absorption spectrometry (FAAS) which is widely used for the determination of metal ions suffers from insufficient sensitivity for direct determination of trace elements in some of the environmental samples.

Various methods have been developed for the preconcentration of trace metals from different samples. These include coprecipitation [2,3], liquid–liquid extraction [4], anodic stripping voltammetry [5], solid–liquid extraction [6] and ion exchange resins [7]. However the solid phase extraction approach has gained rapid acceptance because of its amenability to automation and the availability of wide variety of sorbent phases.

Appropriate chelating reagents can be chemically bonded to or otherwise immobilised on to support matrices, thus providing complexing or chelating solid phases for preconcentration [8]. Silica gel modified with 1-nitroso-2-naphthol [9], 3-aminopropyltriethoxysilane [10], aminopropyl-benzylazo-1-(2-pyridlaz)-2-naphthol [11], 1.8-dihydroxianthraquinone [12] have been used as solid phase extractant for enrichment of trace metal ions.

Other solid materials such as activated carbon [13], green tea leaves [14], naphthalene [15], sepiolite [16] and chelating resins [17] have also been used for separation and preconcentration of trace metal ions.

In this work we propose a simple method for preconcentration of iron with subsequent atomic absorption determination. The method is based on the adsorption of the iron-methylthymol blue complex on tetraocthylammonium bromide supported on naphthalene used as an adsorbent in a column, eluted by nitric acid and determined by FAAS.

2. Experimental

2.1. Reagents

All reagents were analytical grade and used without further purification. The stock solution of 1000 $\mu\mathrm{g\,ml^{-1}}$

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iron was prepared by dissolving 0.8634 g of $NH_4Fe(SO_4)_2$, $12H_2O$ in 100 ml of distilled water containing 10 ml of concentrated hydrochloric acid and was standardised volumetrically [18]. The required concentration of iron solution was prepared by appropriate dilution of the stock solution. A 1.5 M nitric acid solution was prepared by diluting 10 ml of HNO_3 (Merck) to 100 ml in a volumetric flask.

Buffer solution of pH = 3 was prepared by addition of 0.1 M NaOH to 0.1 M formic acid and using pH meter to adjust pH at 3. A 2.15×10^{-4} M of methylthymol blue solution was prepared by dissolving 0.0910 g of methylthymol blue (Merck) in water and diluting to 500 ml in a volumetric flask.

The naphthalene adsorbent solution was prepared by dissolving 25 g of naphthalene and 1 g of tetraoctylammonium bromide in 45 ml of acetone on a hot-plate stirrer at 40 °C. This solution was transferred to 1000 ml of water while stirring the solution at room temperature. It was stirred for 1–2 h and allowed to stand for 30 min. The supernatant solution of naphthalene coprecipitated with tetraocthylammonium bromide was drained off by decantation and washed twice with water in same way. This adsorbent slurry was stored in a bottle for further use.

2.2. Apparatus

A Varian Techtron atomic absorption spectrometer (AA6) was used for the determination of iron. All absorption measurement were performed under the following conditions: wavelength 248.3 nm; acetylene flow rate 4.5 l min^{-1}; air flow rate 7 l min^{-1}; hallow cathode lamp current 5 mA; band pass 0.2 nm and integration time 3 s. All pH measurements were performed using a Metrohm E-632 model digital pH meter with a glass combination electrode.

2.3. General procedure

A funnel tipped glass tube (50 mm length and 5 mm i.d.) with a very fine bore was used as a preconcentration column. It was filled with the adsorbent slurry to a height of 1.5–2.0 cm after slightly pressing the adsorbent in the column with a flat glass rod. Solution (180 ml) containing 25–350 ng ml^{-1} of iron, 4.3×10^{-5} M methylthymol blue and formate buffer solution (pH = 3) was passed through the column at a flow rate of 2 ml min^{-1}. The column packing was then washed with a small volume of water and the naphthalene material was pushed down with a flat glass rod to eliminate the excess water attached to naphthalene. The metal complex was washed with 5 ml of HNO_3 solution (1.5 M). The eluents were collected in a 5 ml volumetric flask, made up exactly to the mark with water and iron determined by FAAS. A blank solution was also run under the same condition without adding any iron.

3. Results and discussion

Methylthymol blue forms a complex with iron (III). The preliminary experiments showed that tetraoctylammonium bromide-naphthalene adsorbent has a tendency to retain this complex. Therefore the retention of iron-methylthymol blue complex on a column containing tetraoctylammonium bromide-naphthalene adsorbent was chosen for preconcentration of iron and its subsequent determination by FAAS.

3.1. Effect of pH

Because the pH of the test solution is one of the important parameters on the recoveries of trace metal ions retained by the adsorbent, therefore the retention of iron was studied as a function of pH. For this purpose the pH values of complex solutions were adjusted in the range of 2–8 with appropriate buffer solutions and the general procedure was followed. The recovery of iron was determined by AAS. The results given in Fig. 1 show that maximum recovery of the iron was obtained at pH = 3. Therefore a formate buffer with pH = 3 was selected for further studies.

3.2. Effect of methylthymol blue concentration

The influence of methylthymol blue concentration on the recovery of the iron was also studied. Different concentration of methylthymol blue were added to a series of 100 ml volumetric flasks containing 250 ng ml^{-1} of iron and the general procedure was followed. It was found that the recovery of the iron was increased with increasing methylthymol blue concentration up to 4.3×10^{-5} M and it was decreased at higher concentration. Therefore methylthymol blue concentration of 4.3×10^{-5} M, which gave highest recovery, was selected as optimum (Fig. 2).

3.3. Effect of nitric acid as the eluent

Nitric acid was chosen as the eluent owing to its effective elution of the adsorbed complex. The effect of

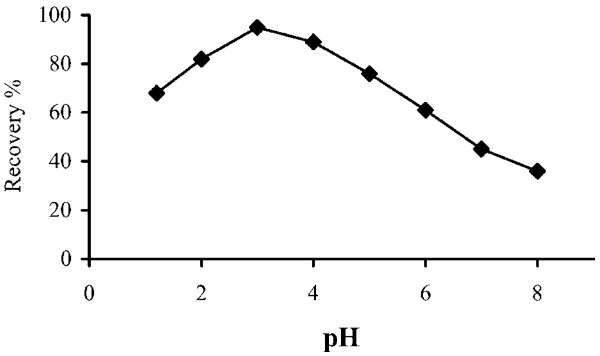

Fig. 1. The effect of pH on the recovery of iron. Conditions: iron concentration 250 ng ml^{-1}; volume of the sample 100 ml; methylthymol blue concentration 4.3×10^{-5} M.

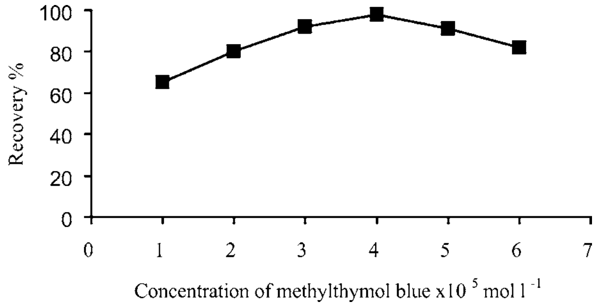

Fig. 2. The influence of methylthymol blue concentration on the recovery of iron. Conditions: iron concentration 250 ng ml^{-1}; volume of the sample 100 ml, pH = 3.

eluent concentration on the recovery of iron (100 ml of 250 ng ml^{-1}) was examined. The recovery increased as the HNO_3 concentration increased up to 1.5 M after which it remained constant. Therefore a nitric acid concentration of 1.5 M was selected for subsequent studies. The volume of the nitric acid was varied from 3 to 10 ml. The volume of 10 ml would not be suitable because it gives a smaller preconcentration factor and 3 ml was not sufficient for the elution, thus 5 ml of nitric acid was chosen for the elution of complex for more convenient.

3.4. *Effect of sample flow rate*

The retention of the complex depends upon the flow rate of sample solution. So the effect of flow rate was examined under optimum conditions by using a pump. The solution was passed through the column with the flow rates adjusted in a range of 1–8 ml min^{-1}. As shown in Fig. 3 the maximum recovery of iron was achieved at the flow rates of 1 and 2 ml min^{-1}. Therefore a flow rate of 2 ml min^{-1} was selected for further work.

3.5. *Effect of sample volume*

In order to determine the volume of the applicable sample solution, the volume of the aqueous phase varied from 10 to 250 ml all containing 63 μg of iron, so that the final solutions would have the same concentrations. It was found that the recoveries were constant when up to 180 ml of the sample solution was used. At the higher volumes the recoveries were decreased. Therefore a preconcentration factor of 36 can be achieved when using 180 ml of the sample and eluting the column with 5 ml of nitric acid.

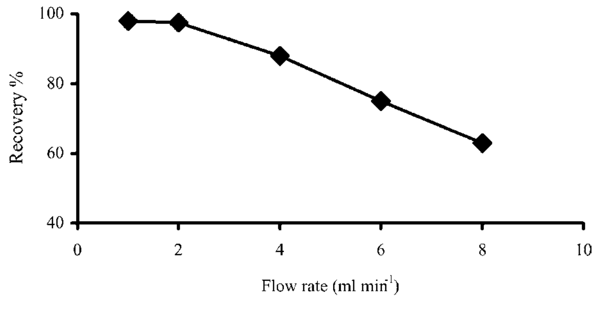

Fig. 3. The effect of sample flow rate on the recovery of iron. Conditions: iron concentration 250 ng ml^{-1}; volume of the sample 100 ml; methylthymol blue concentration 4.3 × 10^{-5} M and pH = 3.

Table 1
The effect of foreign ions on the determination of 100 ng ml^{-1} of iron

Foreign ions	Tolerance ratio (foreign ion concentration/iron concentration)
Na^+, Co^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Ca^{2+}, Bi^{3+}, Al^{3+}, $NH_4{}^+$, K^+, Br^-, $PO_4{}^{3-}$, Cl^-, $NO_3{}^-$, $NO_2{}^-$	1000
In^+, Pb^{2+}, Ba^{2+}, V(IV), V(V), W(VI), $SO_4{}^{2-}$	500
SCN^-, CN^-, F^-, CH_3COO^-	250

3.6. *Analytical parameters*

The proposed procedure can be applied to the preconcentration of iron in the range of 25–350 ng ml^{-1}. The calibration graph was linear in this range with an equation of $A = 5 \times 10^{-4}C + 0.0392$ where C is concentration of iron in ng ml^{-1} of the initial solution (180 ml) with $r = 0.9994$. The concentration range in the final solution is 0.9–12.6 μg ml^{-1} with the equation of $A = 0.0133C + 0.0393$ and $r = 0.9994$. The limit of detection was 12 ng ml^{-1} obtained by the equation LOD = KS_b/m ($K = 3$, m is the slope of the calibration curve and S_b is the standard deviation of ten replicate readings of the reagent blank performed under the general procedure) [19]. The repeatability validation of the method was performed by eight replicate measurements of 150 and 300 ng ml^{-1} of iron in 1 day using general procedure and the relative standard deviations (R.S.D.) were 3.1 and 1.8%, respectively.

3.7. *Effect of diverse ions*

Synthetic solutions containing 100 ng ml^{-1} of iron and various amounts of foreign ions were prepared and the general procedure was followed. The tolerance ratio was defined as the amount of foreign ion causing a change less than 4% in the recovery of iron. Table 1 shows the results. As can be seen a very good selectivity is achieved.

4. Application

The proposed method was applied to the preconcentration and determination of iron content of tap and sewage water samples. The water samples were collected in polyethylene containers and stored in the refrigerator before use. Sample solution (180 ml) was treated under the general procedure. The accuracy of the results was verified by analysing

Table 2
Determination of iron in tap water ($n = 5$)

Iron added (ng ml^{-1})	Iron found[a] (ng ml^{-1})	Recovery (%)
0	25 ± 1.2	–
50	77 ± 3.5	102.6
100	128 ± 4.3	102.4

[a] $x \pm ts/\sqrt{n}$ at 95% confidence.

Table 3
Determination of iron in sewage water samples ($n = 5$)

	Iron added (ng ml^{-1})	Iron found[a] (ng ml^{-1})	Recovery (%)
Sample 1	0	150 ± 3.4	–
	100	255 ± 4.8	102.0
	200	347 ± 5.2	99.1
Sample 2	0	250 ± 4.3	–
	30	282 ± 2.9	100.7
	50	307 ± 4.7	102.3

[a] $x \pm ts/\sqrt{n}$ at 95% confidence.

the spiked water samples. The results reported in Tables 2 and 3 show that good recoveries are obtained.

5. Conclusion

The proposed enrichment method is very selective for the determination of trace amount of iron. The adsorbent is simply prepared by mixing naphthalene and tetraocthylammonium bromide in acetone and applied to the preconcentration of iron. The detection limit is better than some of the previously reported methods [16] and experimental procedure is simpler than some of the others [2]. The linear range of the method is sufficient for the determination of iron in some environmental samples and was successfully applied to the determination of iron in water and sewage water samples with good recoveries.

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