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IRON DETERMINATION AFTER ON-LINE SORBENT PRECONCENTRATION BY FI-FASS USING 1,10-PHENANTHROLINE AS A COMPLEXING AGENT[*]

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Abstract: 1,10-Phenanthroline (phen) was tested as a complexing agent for on-line preconcentration of iron on RP-C_{18} material in a microcolumn with flow injection coupled with flame atomic absorption spectrometer (FI-FAAS). The on-line formed Fe(II)-phen complexes were adsorbed on the C_{18} sorbent material. Various parameters affecting the on-line Fe(II)-phen complex formation and its subsequent adsorption in the microcolumn as well as its elution into the nebulizer of AAS were optimized. A 2.5×10^{-3} mol/L phen in 2% ethanol was on-line mixed with aqueous sample solution acidified with 0.1% (v/v) HCl and allowed to flow through the microcolumn for 30 s. The adsorbed Fe(II)-phen complexes in the microcolumn were eluted with ethanol in 10 s into the nebulizer of AAS. Ascorbic acid (5×10^{-4} mol/L) was added to the sample solution for the reduction of Fe(III) to Fe(II). A good precision (RSD = 1.1%, $n = 10$), high enrichment factor (19) and sample throughput (90 h^{-1}) with detection limit (3σ) of 3 $\mu g/L$ were obtained. The method was applied on standard reference materials(i.e. mussel and tomato leaves,) for iron determination and yielded results agreeing well with certified values.

Key words: iron, flow injection, AAS, on-line sorbent extraction, 1,10-phenanthroline
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INTRODUCTION

On-line separation and preconcentration have received considerable attention in flow injection analysis coupled with atomic absorption spectrometry during recent years and is widely applied for selectivity and sensitivity enhancement (Fang, 1995). Automation of the sample pretreatment and manipulations within the manifold have increased sample throughputs and decreased the potential for sample contamination, which is critical in trace analysis. The complexing agents that have been mostly used for flow injection (FI) on-line preconcentration /sorbent extraction of trace heavy metals using a microcolumn having RP-C_{18} as a sorbent material, are dietyldithiocarbamate (DDTC) (Fang et al., 1990; Sperling et al., 1991b; Sperling et al., 1991c; Sperling et al., 1992; Welz et al, 1992) and ammonium pyrrolidinedithiocarbamate (APDC) (Fang et al, 1991), because of their fast reaction rate with metals and good water solubility. But DDTC is an unstable reagent that decomposes in acidic or neutral solution and has poor selectivity (Ruzicka et al.). The on-line formed metal-DDTC complexes are insoluble in water, and can be adsorbed on the walls of manifold tubing as well as on the C_{18} material in the microcolumn and increases the backpressure in the manifold tubing. This system has not been used for the preconcentration of iron.

Bhttacharrya and Roy (1990) reported a spectrophotometric method for iron determination based on the preconcentration of Fe(II)-phen complex on polyurethane foam, but the method is time consuming as the extraction process is very slow as minimum equilibration time of 150 min is required.

On-line preconcentration methods based on solvent extraction (Backstrom, 1990) and ion

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exchange columns(Hirata et al., 1989; Yebra-Biurrun et al., 1995) had also been developed for the determination of iron but both of them are tedious and time consuming processes and the ion exchange chelating resins are not readily available and their preparation is also not easy.

1,10-Phenanthroline (phen) is a common laboratory reagent and has been mostly used as a chromogenic reagent for spectrophotometric determination of Fe(II) (Bhattachaya et al., 1990; Faizullah, 1985). It had also been used for the speciation of Fe(II) and Fe(III) using various reductants such as ascorbic acid(Bubnis et al., 1983), UV light as a photochemical reductant(Liu et al., 1992), and Vanadium (IV) (Teshima et al, 1996). No attempt has been reported on the use of phen as an on-line complexing agent for the preconcentration of iron in a microcolumn having reverse phase C_{18} material.

This paper presents a fast, sensitive and fully automatic method for iron determination, based on the on-line complexation of Fe(II) with phen, its subsequent adsorption in a microcolumn having C_{18} material and elution of the adsorbed Fe(II)-phen complexes with ethanol into the nebulizer of an atomic absorption spectrometer. Ascorbic acid has been used for the reduction of Fe(III) to Fe(II). As phen is weakly soluble in water but highly soluble in ethanol; a small amount of ethanol (2% v/v) can be used to solublize phen in water. The method so developed has been applied to standard reference materials i.e. mussel (GBW 08571) and tomato leaves (NBS-1573), for the determination of iron and the results were in good agreement with the certified values.

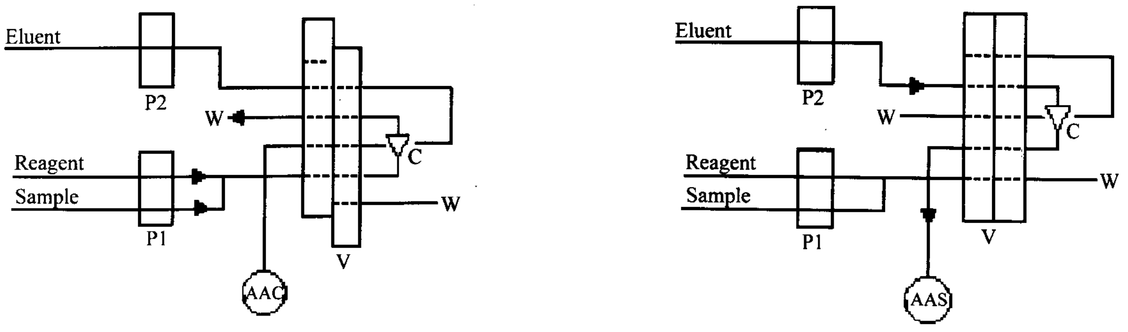
EXPERIMENTAL

Apparatus

A Shimadzu model A-670 atomic absorption spectrometer equipped with deuterium-arc background correction was used throughout. Hollow cathode lamp was used for the iron determination at primary resonance line i.e. 248.3 nm. A flame condition leaner in fuel than recommended was chosen to compensate for the effect of the organic solvent used for elution and additional fuel. The other instrumental conditions as recommended by the manufacturer were used.

A CK Chrom data system from Chrom King, U.K, was installed in a 486 computer for the acquisition and analysis of time resolved signals. The peak height was used for data evaluation.

A flow injection accessory Zhoufa processor model LZ-2000 (China) equipped with two peristaltic pumps and one 8-channel rotary valve, controlled by an in-built computer for their operation, was used. Tygone tubes were used for sample loading and for propelling the complexing reagent. Solvent resistant Isoversinic pump tubes (Gilson) were used for propelling the ethanol as eluent. The FI on-line preconcentration manifold used is illustrated in Fig. 1.



(a) (b)

Fig. 1 FI manifold for on-line sorbent extraction/ preconcentration of Fe(II) using 2.5×10^{-3} mol/L phen in 2% ethanol solution.

(a) Fi manifold for the preconcentration step; (b) FI manifold for the elution step
P1 & P2 = peristaltic pumps, C = preconcentration microcolumn, W = waste,
V = 8-channel multifunctional valve, AAS = Flame atomic absorption spectrophotometer

The microcolumn for sorbent extraction/ preconcentration was prepared as described elsewhere(Sperling et al., 1991a). Sample and reagent were on-line mixed and flowed from the narrower end of the column to the broader end, and the eluent flowed through it in the reverse direction to minimize the dispersion. The column was connected to the 8-channel valve, and the valve to the nebulizer, with a straight, 6 cm long, 0.35 mm i.d. PTFE tubing.

Reagents

All the reagents used were of Analytical Reagent (AR) grade. Deionized-distilled water (DDW) was used throughout the experimental work.

1,10-Phenanthroline (phen) from the Shanghai Chemical Company was used as such without further purification. Phen solution was prepared by dissolving the weighed amount in a minimum amount of ethanol (2 mL) and then diluted with DDW to 100 mL solution. Standard solutions of Fe(II) were prepared daily by stepwise dilution of 1000 mg/L stock solution using 0.1% HCl solution and 0.1 mg/mL ascorbic acid was added to keep the iron in Fe(II) state. The stock solution was prepared by dissolving the weighed amount of ammonium ferrous sulfate in 0.1 % HCl.

The Standard Reference Materials (SRMs) i.e. Mussel (GBW 08571) were obtained from the State Oceanic Administration, Hangzhou, China, tomato leaves (NBS-1573) from the National Bureau of Standards, USA.

Ethanol was degassed before use to prevent the formation of air bubbles in the stream during elution, which would degrade the precision.

Preconcentration method

The complete cycle of preconcentration of Fe(II)-phen complex on the RP-C_{18} material as solid sorbent is shown in Table 1, and consists of two steps.

In step 1, the phen solution in 2% ethanol was on-line mixed with the sample solution (acidified with HCl, so that the pH of the mixed solution at the confluence point should be 4 to 6) and flowed through the microcolumn to keep the 8-channel valve (V) at load position. The peristaltic pump-1 (P1) was used for the propulsion of both solutions for 30 s. In this step, the on-line formed Fe(II)-phen complex was adsorbed in the microcolumn.

In step 2, the 8-channel valve was set to inject position and the adsorbed Fe(II)-phen complexes in the microcolumn were eluted into the AAS's nebulizer by running pump-2 (P2). The absorption signals were recorded and processed by the computer.

Table 1 Sequence of on-line sorbent extraction preconcentration operation

Figure	Step	Time (s)	Flow rate pump-1 mL/min	Flow rate pump-2 mL/min	Position of 8-channel valve	Medium pumped	Stage of operation
1a	1	30	5.2	0	Load	Sample	Column
			5.2			Phen	loading
1b	2	10	0	2.0	Inject	Ethanol	Column elution

RESULTS AND DISCUSSION

Selection of counter-ion

Microcolumn containing RP-C_{18} material can only adsorb uncharged non-polar compounds, or more precisely hydrophobic ones(Cuculic et al., 1997). $[Fe(phen)_3]^{2+}$ forms lamge size ion-pair compounds such as ClO_4^-, SCN^-, which can be extracted into organic solvents and increase the sensitivity for iron determination(Sandell et al, 1978). Thus, an attempt was made to transform $[Fe(phen)_3]^{2+}$ into an ion-pair compound with anions such as, Cl^-, SO_4^{2-}, ClO_4^-, SCN^-, CH_3COO^-, and tetraphenylborate (TPB) ion, by the addition of their sodium salt (0.1 mol/L) into the iron solution. The result showed that only TPB yielded white precipitate on mixing with phen solution, which caused high backpressure that choked the column. The other anions yielded no precipitate on mixing with $Fe(phen)_3^{2+}$ and the backpressure in the tubing was also not increased. But these anions caused no significant effect on the enrichment factor of iron. This can be explained in the light of solvophobic theory(Horvath et al., 1976). According to this theory, the solute particles are attached to the C_{18} material through the hydrophobic part of the solute particle by hydrophobic interactions. Therefore, it can be suggested that the Fe(II)-phen complex might have adsorbed on the C_{18} material through phen (hydrophobic part of Fe(II)-phen complex) by hydrophobic interactions. As the counter-ion has no important role in the adsorption process, its effect is less significant in the enrichment of Fe(II)-phen complexes. This view is further strengthened by the experimental fact that absorbance was lowered by increasing the ethanol content in the phen solution (hydrophobic interactions decreased by increasing the ethanol content) as shown in Fig.2.

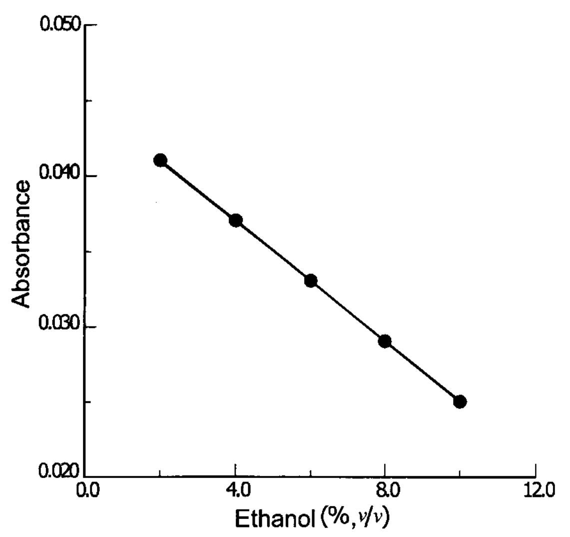


Fig.2 **Dependence of absorbance on the ethanol content in the phen solution**

Optimization of the on-line derivatization /preconcentration system

In our preliminary experiments, the preconcentration of Fe(III) (100 μg/L to 500 μg/L) was also carried out using 30 sec preconcentration time at pH 4-6 but no peak was abserved. The reason may be the kinetically slow reaction between Fe(III) and phen {log $\beta_3 = 14.1$ for Fe(III) and 21.2 for Fe(II)} (Sandell et al, 1978). On the contrary, Fe(II) can be on-line complexed with phen that adsorbed in the preconcentration microcolumn. Therefore, to keep the iron in Fe(II) state, various amounts of ascorbic acid (0.1 mmol/L to 1 mmol/L) were added to the 100 μg/L iron solution and the effect on the absorbance was determined. No significant effect was observed in the whole range, although, 0.5 mmol/L ascorbic acid was added to keep the iron in Fe(II) state during the whole experimental work.

pH is a very important factor for on-line preconcentration of the metal complexes. Therefore, its effect on Fe(II)-phen complex formation was studied. Fig. 3 shows the effect of pH of the mixed solution at the confluence point, which can be measured in the effluent, on the absorbance. It shows that pH 4 – 6 is the optimum range for Fe(II)-phen complex formation. Therefore, pH 4 – 6 was maintained in the further experimental work.

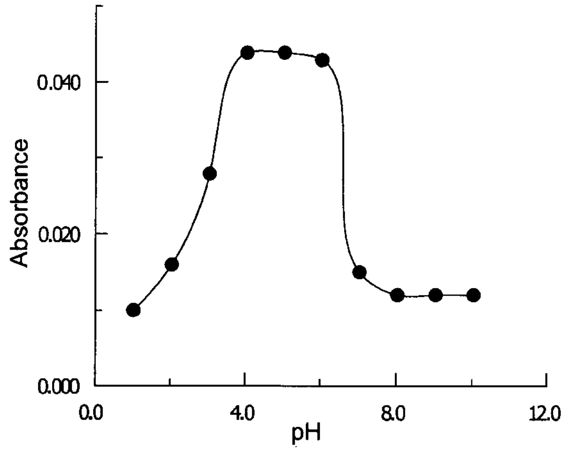


Fig.3 **The influence of pH on the preconcentration of Fe(II) using 2.5 mmol/L phen solution**

The effect of phen concentration on the preconcentration of Fe(II) is illustrated in Fig.4. The absorbance increased linearly when the phen concentration was increased from 0.1 mmol/L to 1 mmol/L. Fig. 4 shows that from 1 mmol/L to 5 mmol/L phen, the variation in the absorption is negligible and decreased by further increase to 10 mmol/L. This decrease may be due to the competition between phen and Fe(II)-phen complex for the adsorption on the C_{18} material in the microcolumn. A 2.5 mmol/L phen concentration was selected for further experimentation.

As phen is slightly soluble in water but highly soluble in ethanol, a small amount of ethanol was used to dissolve phen in DDW. Fig. 2 shows the effect of ethanol content in the phen solution on the preconcentration of iron. The ethanol content affects the signal height inversely and is lin-

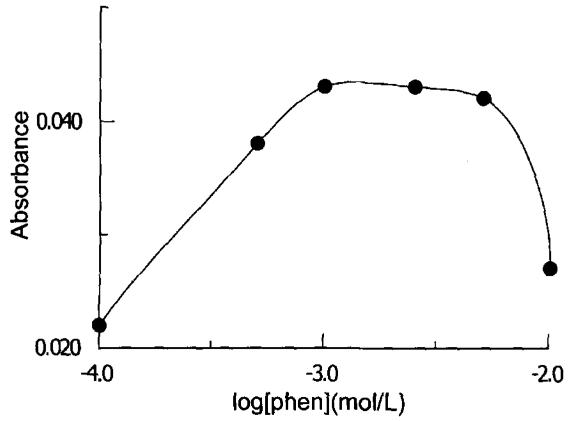


Fig.4 Effect of phen concentration on the preconcentration of iron

ear up to 10% ethanol (the maximum ethanol concentration studied). Therefore, 2% ethanol was maintained in the phen solution.

Fang et al. (1991) pointed out that the reaction coil length had significant effect on the enrichment factor. So, its effect on the preconcentration of iron was also studied. Reaction coils of different lengths i.e. 8 cm, 18 cm, 48 cm and 100 cm, were used but no significant effect was observed. This shows that the reaction between Fe(II) and phen is very fast. Therefore, shortest possible reaction coil length (8 cm) between the confluence point and the 8-channel valve (V) was used.

Elution rate is equally important for good precision and better sensitivity (Fang et al., 1991). The elution flow rate was varied from 1.0 mL/min to 2.6 mL/min and its effect on the signal height was determined. The absorbance increased with the increase in the flow rate reaching maximum at 1.8 mL/min. There was no significant change in the absorbance from 1.8 mL/min to 2.2 mL/min but decreased by further increase in the flow rate. Therefore, 2.0 mL/min elution rate was selected because at this flow rate 10 sec was found to be sufficient for quantitative elution of adsorbed Fe(II)-phen complexes in the microcolumn and the peak shape was also good as shown in Fig. 5.

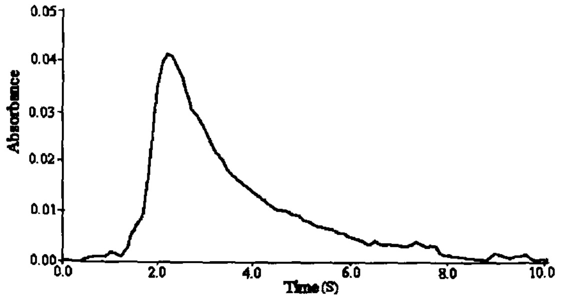


Fig.5 The elution curve of the Fe(II)-phen complex

Test of the effect of sample loading rate (2.8 mL/min to 7.6 mL/min) on the preconcentration process showed that the absorption increased linearly up to 5.2 mL/min and deviated from linearity by further increase in the loading time; but that the backpressure in the manifold tubing was not increased. So, 5.2 mL/min sample loading rate was used in our experimental work.

The sample loading time was varied from 30 s to 300 s using the optimized conditions for 100 μg/L iron and the absorbance was recorded. The preconcentration response of the column was found to be linear up to 150 s, after which it deviated from linearity but there was no rise in the backpressure in the manifold tubing.

Calibration curve

Using the optimized conditions of preconcentration and elution, a calibration curve was prepared for varying amounts of iron (0 – 300 μg/L) against the absorption and was found reasonably linear. The equation of linearity is as follow:

$$A = 0.00043 \times C + 0.0016 \quad r = 0.9995$$
$$n = 18$$

All the statistical calculations are based on the average of triplicate readings for each standard solution.

Interference

The tolerance for various co-existing metals was examined by adding relatively high concentrations of various metal ions to 100 μg/L iron. The cations like, Na(I), K(I), NH_4(I), Ca(II) and Mg(II) could be tolerated up to 0.1 mol/L. The metal ions, like Ni(II), Pb(II), Mn(II) and Bi(III) could be tolerated up to 5 mg/L. Co(II), Cd(II) and Zn(II) could be tolerated up to 1mg/L but interfered at higher concentration i.e. 5 mg/L, and lowered the signal height 18%, 23% and 18%, respectively. The reason for the interference caused by these metal ions may be their competition for the complex formation with phen and the binding sites for the adsorption on the C_{18} material.

The performance of FI-AAS system

At the optimized conditions, the performance of the FI-AAS system for the preconcentration of iron using 1, 10-phenanthroline as complexing agent and ethanol as eluent is shown in Table 2. Good precision (RSD = 1.1% for $n = 10$) and high enrichment factor (19 for 2.6 mL sample) and large throughput (90) was obtained.

Table 2 Performance of the FI-AAS system for preconcentration of iron.

Enrichment factor	19
Detection limit(μg/L)	3
Characteristic concentration	10.2
Precision ($n = 10$, % RSD)	1.1
Sample throughput (h^{-1})	90
Sample consumption (mL)	2.6
Reagent consumption per sample (mL)	2.6
Ethanol consumption per sample (mL)	0.3

Analysis of Standard Reference Materials

The method so developed was applied on the standard reference materials (SRM) i.e. mussel (GBW08571) and tomato leaves (NBS-1573) for the determination of iron.

The SRM samples were dried in an oven at 80 ℃ to constant weight. A 0.5000 g sample was dissolved in 10 mL concentrated nitric acid and 5 ml hydrogen peroxide in a 250 mL Pyrex beaker on a hot plate (250 - 300 ℃). Hydrogen peroxide was added in small portions to destroy the organic matter until the solution became clear. Then, the solution was heated to near dryness and on cooling, the contents of the beaker were transferred into a 100 mL measuring flask with small portions of 0.1% HCl and the volume was made up with 0.1% HCl. Ascorbic acid (10 mg) was added to reduce the Fe(III) to Fe(II). A blank was also prepared using the same way. The results are tabulated in Table 3, which show that our results are in good agreement with the certified values.

Table 3 Results of the analyses of standard reference materials (SRMs)

SRMs	Certified value(μg/g)	Determined value (μg/g)	Deviation %
Mussel	221 ± 14	218 ± 9	-1.4
Tomato leaves	690 ± 25	692 ± 31	0.3

CONCLUSION

The results presented in this work demonstrate the suitability of 1,10-phenanthroline as a complexing agent for on-line sorbent extraction/preconcentration of Fe(II) on a RP-C_{18} sorbent material in a microcolumn. The proposed method is quick (sample throughput; 90 h^{-1}), sensitive (detection limit; 3 μg/L) and fully automatic. The precision and the good agreement of the analytical results of iron with the certified values for the standard reference materials e.g. mussel and tomato leaves, show the reliability and accuracy of the method.

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