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A New Reagent for Solid Phase Extraction and Atomic Absorption Determination of Trace Amount of Fe(III) in Water Samples

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A solid phase extraction method was developed for the preconcentration of Fe^{3+} in water samples prior to it determinations by flame atomic absorption spectrometry using 2,2´-diamino-4,4´-bithiazole (DABTZ) as a new ligand. For this, metal complex with DABTZ was retained on the column. The retained analytes on the column were recoverd with 2.5 mL of methanol. Fe^{3+} in effluent was determined by atomic absorption spectrometry. The optimum preconcentration conditions have been investigated such as concentration and type of buffer, the effect of pH, type of elution solvent and eluent flow rate. The obtained recovery was nearly 85-93 by elution of the column octadcyl silica cartridge with minimal amount of solvent and concentration factor of 160 achieved by passing 400 mL of sample through the column. The relative standard deviation (3 replicate analyte) 1.90 % was obtained. The limit of detection, sensitivity and correlation coefficient of the proposed method are 2 ppm, 0.05 ppm and 0.992, respectively.

Key Words: Fe^{3+} ion, 2,2´-Diamino-4,4´-bithiazole, Flame atomic absorption spectrometry, Solid phase extraction.

INTRODUCTION

Analytical separation techniques play central role in today's analytical chemistry. They are typicaly used to improve the sensitivity and selectivity of trace analyses by replacing the original sample matrix with a new non-interfering one. The enrichments technique has often been used to collect trace elements on solid surface[1]. Solid phase extraction (SPE) is a preconcentration technique of rapidly growing importance in trace metal determination with atomic absorption spectrometers[2].

Recently, the solid phase extraction cartridges and disks were widely and successfully used for the preconcentration and separation of trace metal

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ions from different matrixes[3-10]. The solid phase extraction is an attractive technique that reduces solvent usage exposure, matrix elimination, disposal costs, extraction time and environmental problem[11].

Many methods have been developed for preconcentration of trace metals from natural waters. These include coprecipitation[12], electrodeposition, ion exchange technique[13,14], liquid-liquid extraction[15,16], filtration and sorption. Adsorption of complexed metals on various sorbents, such as activated carbon (AC)[17], amberlite XAD[18], silica gel[19] and other sorbents[20], have been applied to preconcentration of metals from water samples. The basic principle behind the solid phase extraction involve passing the water sample through cartridge or a tube containing on adsorbent that retains the analytes. The analytes are eluted from the adsorbent using a suitable solvent[21].

In this paper, a column octadecyl silica cartridge and 2,2′-diamino-4,4′-bithiazole (DABTZ) ligand as a new chelating agent (Fig. 1) using for the preconcentration of trace amounts Fe^{3+} in water samples for determination by flame atomic adsorbent spectrometry. However in spectrophotometric methods a preconcentration step is generally necessary in order to increase their sensitivities for most sample.

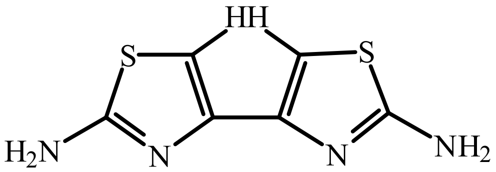

Fig. 1. 2,2′-Diamino-4,4′-bithiazole (DABTZ)

EXPERIMENTAL

A GBC 902 model flame atomic absorption with HCL-lamp was used to determine Fe(III) ion. A air-acetylene flame with 10.5 cm burner hight, 0.2 nm spectral bound width, the wavelength 248.3 nm and the lamp currents 7.0 mA were the measuring condition. The pH measurements were performed with a 420 A model orion digital pH-meter.

2,2'-Diamino-4,4'-bithiazole ligand was prepared from 1,4-dibromobutane-2,3-dione and thiorurea by method of Erlenmeyer and ueberwasser[22]. Fe^{3+} stock solution was prepared by dissolving the appropriate amount of $Fe(NO_3)_3$ (Merck 99.5 %). All solvents were of the highest purity available (Merck) and were used as received.

Procedure: Extraction was performed with C_{18} cartridges containing 500 mg octadecyl silica (50 μm particles size 60 A pore size) from Macherey-Nagel Co. (Puren, Germany). The cartridges were used in conjunction with a proper vacuum apparatus. Before each extraction, the cartridge was washed with 5 mL methanol and 10 mL water.

The performance of the cartridge was tested with a model solution prior to its application to water samples. For this, 15 mL of the model solution containing 0.33 ppm of Fe^{3+} and 2.32 ppm of ligand was prepared in double distillated water. The resulting solution was loaded on to cartridge. The flow rate of the sample solution through the column was adjusted in 15 mL min^{-1} by applying vacuum. After passage of the solution, the retained Fe^{3+} were eluted from the cartridge by 2.5 mL methanol. Fe^{3+} concentration in the effluent was determined by flame atomic adsorption spectrometer.

RESULTS AND DISCUSSION

The DABTZ is an electron-donating base, which is soluble in water/ methanol mixture (0.0099267 g in mixture 20:80 methanol water). Recent studies revealed that it can form a fairly stable and selective 1:1 (M(DABTZ)) and 1:2 (M(DABTZ)) complex with M(II) ion[23]. It has a pair of nitrogen atoms located in a position that allows each to form a covalent bond with M^{2+} ion preconcentration of this elements for accurate measurement. It concentration is very important considering the fact that the DABTZ ligand can produce stable complex with Fe^{3+}. Thus, it is decided to examine the DABTZ ligand as a suitable reagent for the preconcentration of Fe^{3+} *via* solid phase extraction, by using octadecyl silica cartridges. Some preliminary experiments showed that while the cartridge does not show any tendency for the retention of ion in the absence of ligand, it is capable of retaining the Fe(III) DABTZ complex in the sample solution.

To obtain quantitative recoveries of Fe^{3+} on cartridge, the preconcentration procedure was optimized for various parameters such as sample matrix, amount of ligand, type of eluent for elution, flow rates and break though volume. The percentage of retained Fe^{3+} was calculated from the amounts of Fe^{3+} in the starting sample and the amounts of Fe^{3+} eluted from the column.

Amount of ligand: The amount of ligand plays an important role in obtaining quantitative recoveries of Fe^{3+}, because in its absence the cartridge does not retain the Fe^{3+}. Therefore, the influence of the amount of ligand on the recovery of the Fe^{3+} was investigated in the range of 0.58-4.64 ppm using the model solution given above. The obtioned results showed, the recoveries of Fe increased when increasing the amount of ligand added and reached a constant value of over 90.5 % with at least 2.32 ppm of ligand (Fig. 2).

Effect of pH: The influence of pH on the solid phase extraction of the Fe^{3+} complex was studied. For this prepared 250 mL metal-ligand complex solution contain 0.33 ppm of Fe^{3+} and 2.32 ppm DABTZ ligand.

Then pH solution adjusted with NaOH and HCl in range 2.5-8.0. A good recovery was performed between 3.5-7.0. The pH should not to be below 3, because protonation of DABTZ by H^+ and decreasing tendency coordination with Fe^{3+}. In addition, it shoud not above 7.5, because formation of metal hydroxide and the decrease of the C_{18} cartridge stability (Fig. 3).

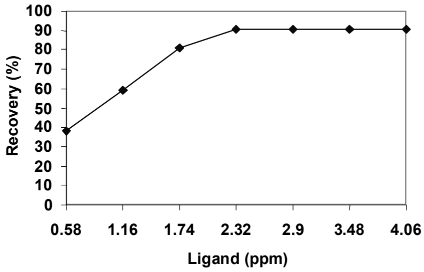

Fig. 2. Effect of amount of ligand

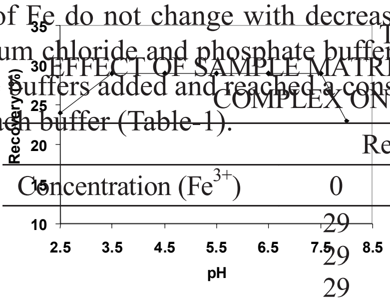

Fig. 3. Effect of pH

Effect of sample matrix: The effect of sample matrix on the retention of metal-ligand complex on the cartridge was studied by applying the proposed procedure to the model solution prepared by added buffers acetate, formate, phosphate and potassium chloride in the range of concentration 0-0.033 M. The recoveries of Fe do not change with decrease or increase of concentration of potassium chloride and phosphate buffer but it increased when acetate or formate buffers added and reached a constant value of over 90 % in 0.025 M of each buffer (Table-1).

TABLE-1

EFFECT OF SAMPLE MATRIX ON RECOVERY OF Fe^{3+}-LIGAN

COMPLEX ON THE C_{18} CARTRIDGE

	Recovery (%)				
Concentration (Fe^{3+})	0	0.0083	0.017	0.025	0.
	29	58.0	79.0	90.0	9
	29	55.0	78.0	90.0	9
	29	33.0	33.0	33.0	3
	29	33.5	33.5	33.5	3

Condition: The sample solution was 0.33 ppm Fe^{3+}, 2.32 ppm of DABT

Choice of Eluent: The elution solvent is very important in the solid phase extraction method. In order to choose a proper eluent for the retained Fe^{3+} complex, after its extraction from water, the complex was stripped with varying volumes of water, methanol, ethanol and 2-propanol. From the data given in Table-2, it is obvious that 2.5 mL methanol, ethanol or 2-propanol can accomplish the quantitative elution of the complex.

TABLE-2
EFFECT OF TYPE AND AMOUNT OF ELUENT ON EXTRACTION EFFICIENCY

	Recovery (%) (mL)			
	1.5	2.5	3.5	4.5
Water	19.0	32.0	32.0	33.0
Metahnol	74.0	91.5	91.5	91.5
Ethanol	74.5	91.5	91.5	91.5
2-Propanol	74.0	91.5	91.5	91.5

Condition: The sample solution was 0.33 ppm Fe^{3+}, 2.32 ppm of DABTZ and 0.025 M acetate buffer.

Effect of flow rates: The effect of flow rates of the sample and stripping solvent from the C_{18} column on the retention and recovery of Fe^{3+} investigated. It was found that, in the range of 1-6 mL min^{-1} the retention of the Fe^{3+} complex by C_{18} cartridge wasn't considerably affected by the sample solution and stripping solvent flow rate.

Effect of diverse ions: Selective extraction of Fe^{3+} in the presence of foreign ions were investigated. An 20 mL different aqueous solution cantaining 0.33 ppm of Fe^{3+} and 2.32 ppm DABTZ ligand and amounts of other ions were taken and the above procedure was followed. The results summarized in Table-3 clearly indicate that Fe^{3+} are retained quantitatively by the DABTZ ligand. Most of the tested ions do not interfere in the extraction Fe^{3+}.

TABLE-3
EFFECT OF FOREIGN ION ON EXTRACTION EFFICIENCY

Foreign ion (ppm)	Fe (ppm)	Recovery (%)
K^+ (26.70)	0.33	90
Na^+ (52.80)	0.33	91
Li^+ (1.75)	0.11	88
Ca^{2+} (1.20)	0.11	88
Ba^{2+} (0.54)	0.11	89
Sr^{2+} (2.75)	0.11	88
CH_3COO^- (1361.80)	0.33	91
$HCOO^-$ (30.80)	0.33	90
Cl^- (24.30)	0.33	89
PO_4^{3-} (2208.00)	0.33	89
NO_3^- (7.70)	0.33	90

Condition: The measurement was performed at optimum effective parameters.

Analytical performance: The effect of the break through on the adsorption of the Fe complex was studied by passing sample volume of

10-35 mL containing 0.33 ppm Fe^{3+} and 2.32 ppm DABTZ. The results clearly indicate that the break through volume is 25 mL of sample. The maximum capacity of the cartridge was determined by passing 15 mL of sample solution in range 0.33-1.63 ppm of Fe^{3+} and 2.32-11.6 ppm of DABTZ through the cartrigde and followed by determination of the retained ions using atomic absorbtion spectrometry. The maximum capacity of the cartridge was found to be 1.39 ppm of Fe^{3+}.

Conclusions

The proposed method has a few advantges compared with previously reported procedures for extraction and determination of Fe^{3+}. This method is simple, highly sensitive, selective, reproducible and relatively rapid. The total time for determination of Fe^{3+} in a 400 mL water sample is *ca.* 16 min. The consumption of organic solvent in the proposed method is much lower compared to that in common liquid-liquid extraction methods. It is interesting to note that in this method Fe^{3+} concentrated by a factor *ca.* 160. The method has been successfully applied to separation and determination of Fe^{3+} in real sample. Table-4 shows the results of extraction of added Ni^{2+} from tap water.

TABLE-4
DETERMINATION OF Fe^{3+} IN TAP WATER

Added ligand (ppm)	Added Fe^{3+} (ppm)	Eluent (mL)	Recovery (%)	RSD (%)
0.13	0.017	1.8	89.0	2.07
0.25	0.035	2.5	88.0	2.05
0.37	0.053	3.5	89.8	1.53

Condition: The measurement was performed at optimum effective parameters.

REFERENCES

1. Y.P. Pena, M. Gallego and M. Valcarcel, *Talanta*, **42**, 211 (1995).
2. A.M. Naghmush, K. Pyrzynska and M. Trojanowicz, *Talanta*, **42**, 85 (1995).
3. R. Lima, K.C. Leandro and R.E. Santelli, *Talanta*, **43**, 997 (1996).
4. M. Groschner and P. Appriou, *Anal. Chim. Acta*, **297**, 369 (1994).
5. M.R. Compano, M. Granados, C. Leal and M.D. Prat, *Anal. Chim. Acta*, **283**, 272 (1993).
6. M.F. Garcia, R.P. Garcia, N.B. Garcia and A. Sanz-Medel, *Talanta*, **41**, 1833 (1994).
7. M.B. Shabani, T. Akagi and A. Masuda, *Anal. Chem.*, **64**, 73 (1992).
8. Z.S. Liu and S.D. Huang, *Anal. Chim. Acta*, **267**, 737 (1992).
9. Y. Yamini, N. Alizadeh and M. Shamsipur, *Sep. Sci. Tech*. **632**, 2079 (1997).
10. Y. Yamini, N. Alizadeh and M Shamsipur, *Anal. Chim. Acta*, **355**, 69 (1997).
11. C. Markell, D.E. Hageh and V.A. Bunnelle, *LC-GC*, 9 (1990).
12. R. Eidecker and E. Jacwerth, *Fresenius J. Anal. Chim.*, **328**, 469 (1987).
13. T. Kiriyama and R. Kuroda, *Fresenius J. Anal. Chim.*, **332**, 338 (1988).
14. J. Kubova, V. Neveral and V. Stresko, *J. Anal. Atom. Spectrom.*, **9**, 241 (1994).

15. S.C. Nielsen, S. Sturup, H. Spliid and E.H. Hansen, *Talanta*, **49**, 1027 (1999).
16. A.R.K. Dapaah, N. Takanon and A. Ayame, *Anal. Chim. Acta*, **386**, 281 (1999).
17. M. Solylak, I. Narin and M. Dogan, *Anal. Lett.*, **30**, 2801 (1997).
18. M. Solylak, U. Sahin and L. Elci, *Chim. Acta*, **322**, 111 (1996).
19. AR. Sarkar, PK. Data and M. Sarkar, *Talanta*, **43**, 1857 (1996).
20. E. Beinrohr, A. Manova and J. Dzurov, *Fresenius J. Anal. Chem.*, **355**, 528 (1996).
21. R. Devvi and G.R.K. Naidu, *Analyst*, **115**, 1469 (1990).
22. Erlenmeyer and H. Ueberwasser, *Helv. Chim. Acta*, **23**, 1268 (1940).
23. A. Morsali, M. Payheghader, M.R. Poorheravi and F. Jamali, *Z. Anorg. Allg. Chem.*, **629**, 1627 (2003).

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