TECHNICAL NOTE

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Flame atomic absorption spectroscopy (FAAS) determination of iron(III) after preconcentration on to modified analcime zeolite with 5-((4-nitrophenylazo)-*N*-(2′,4′-dimethoxyphenyl))salicylaldimine by column method

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Received 19th October 2004, Accepted 16th March 2005
First published as an Advance Article on the web 6th April 2005

A column solid phase extraction (SPE) and preconcentration method was developed for the determination of Fe(III) ion in aqueous samples by flame atomic absorption spectrometry. The method is based on sorption of Fe(III) ions on natural Analcime Zeolit column modified with a new Schiff base, 5-((4-nitrophenylazo)-*N*-(2′,4′-dimethoxyphenyl))salicylaldimine (L), and then eluted with 0.1 M EDTA and determined by FAAS. Various parameters, such as the effect of sample pH, flow rate, volume of the sample and interference of the metal ions on the method, to optimize the conditions for determination of Fe(III) ions in aqueous samples, were studied. The recoveries were >99%. The developed method was applied to the determination of trace Fe(III) ions in drinking water and river water samples with satisfactory results.

Introduction

Several sensitive methods have been developed for the determination of metal ions. Because of the relatively simple and inexpensive equipment required, flame atomic absorption spectrometry (FAAS) has been widely used for determination of trace metal ions.[1–3] However, the direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences. Therefore, a preliminary preconcentration step is necessary to improve the detection limit and selectivity for their determination by FAAS. For this purpose, several methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the concentrations of the analytes and the measurement techniques.[1,2] There include ion exchange,[4] solvent extraction[5] and solid phase extraction (SPE).[6,7] Among the various preconcentration methods, SPE is one of the most effective procedures for trace metal analysis because it is an attractive technique that reduces consumption and exposure to solvent, disposal costs and extraction time.[8,9] The methods which involve complexation of the metal ion with chelating agents followed by adsorption on a solid phase such as octadecylsilane, chemically bonded silica gel (ODS),[10,11] activated carbon,[12] ion-exchange resins,[13,14] chelating resins,[15] zeolites[16] and various polymers have been used as solid-phase material for SPE. Recently, octadecyl bonded silica SPE disks have been utilized for the extraction and analysis of many different organic and environmental matrices.[17,18] We have recently reported the use of this method for extraction and preconcentration of trace amounts of Ag^+ ions from aqueous solutions.[19]

The Schiff bases derived from salicylaldehyde (salen) as polydentate ligands are known to form very stable complexes with transition metal ions.[20] Schiff base complexes of transition metals have been frequently used as catalysts in such diverse processes as oxygen and atom transfer, enantioselective epoxidation and aziridination, mediating organic redox reactions and as mediator in other oxidation processes.[20,21]

The aim of this work was the development of a rapid, highly sensitive and efficient method for the selective extraction and concentration of trace amounts of Fe^{3+} ions from aqueous media using a natural Analcime Zeolite column modified with ligand L (scheme 1) and its determination by FAAS.

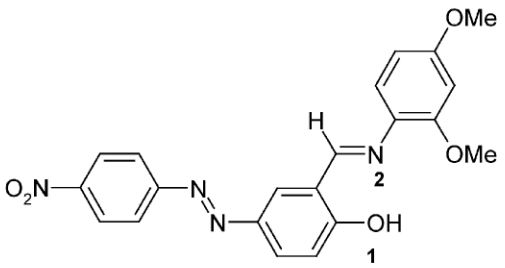
Experimental

Reagents and solutions

Analytical grade metal salts and solvents (methanol, dimethylformamide and acetonitrile) were obtained from the Merck Company. All solutions were prepared with double distilled, deionized water. Standard solutions (1000 mg L^{-1}) of the elements were prepared from appropriate amounts of nitrate salts in 1% HNO_3 and further diluted daily prior to use. The Schiff base ligand (L) was prepared as reported in the literature by condensation reaction between a precursor ligand with 2-methoxy-3-nitroaniline in hot ethanol.[22] Zeolite was sieved to obtain a particle size of < 150 μm (200 mesh) and washed with 4 M hydrochloric acid and distilled water to reach a neutral pH: the material was then dried at 110 °C in an oven and stored in a desiccator.

Apparatus

The determinations of iron(III) were carried out on a Varian spectra AA220 atomic absorption spectrometer under the recommended conditions for each metal ion. A digital pH meter Metrohm model 632, equipped with a combined glass calomel electrode, was used for the pH adjustments.



Scheme 1 The structure of 5-((4-nitrophenylazo)-*N*-(2′,4′-dimethoxyphenyl)salicylaldimine Schiff base ligand (**L**).

DOI: 10.1039/b416097e

Table 1 Percentage recovery of iron from the modified column[a]

Stripping agent	Recovery (%)
KSCN	47 (±1)
Thiourea	35.6 (±0.5)
1,10-Orthophenanthroline	48.0 (±0.5)
HCL	64 (±1)
$Na_2S_2O_3$	71.3 (±0.8)
EDTA (0.01 M)	77.3 (±0.6)
EDTA (0.05 M)	85.6 (±0.5)
EDTA (0.1 M)	100.0 (±0.8)

[a] Initial samples contained 2.5 μg Fe^{3+} ion in 50 ml of water.

Sample extraction

All experiments were done in a glass column (100 mm × 10 mm) which was plugged with glass wool. Analcime Zeolite (1.00 g) was added to the column pre-washed with methanol (5 ml) and was then saturated with reagent by passing 2 ml of ligand solution (2.5 mg ml^{-1} in DMF) through at a flow rate of 0.5 ml min^{-1}.

Later, the column was washed with 25 ml of water, then 50 ml of the sample solution containing 2.5 μg of Fe^{3+} was passed through (flow rate = 1 ml min^{-1}). After the extraction, the column was washed with 10 ml of water, subsequently eluted with 10 ml of 0.1 M EDTA solution and the iron content determined by a FAAS method.

Results and discussion

The ligand L is a bidentate ligand with N, O-donated sites with O (1 in scheme 1) and N (2 in scheme 1) atoms, which is insoluble in water. A theoretical study shows that the **L** Schiff base ligand is a bidentate ligand and forms stable complexes with some transition metals, including Fe^{3+} ions.[22] Therefore we decided to examine its capability as a suitable reagent for preconcentration and separation of metal ions *via* solid phase extraction by modified Analcime Zeolite column.

Some preliminary experiments were carried out in order to investigate the quantitative retention of Fe^{3+} ions by the column in the absence and presence of the ligand. It was found that the column including Analcime Zeolite itself did not show any tendency to retain Fe^{3+} ions, while the modified column with ligand was capable of retaining Fe^{3+} ions in the sample solution.

Choice of eluent

In order to choose a proper eluent for the retained Fe^{3+} ions, after the extraction of 2.5 μg of Fe^{3+} ions from 50 ml of solution by the column, the Fe^{3+} ions were stripped with 2 × 5 ml of different concentrations of various eluting solutions. From the results shown in Table 1 it is obvious that 0.1 M EDTA used can strip the retained Fe^{3+} ions almost quantitatively.

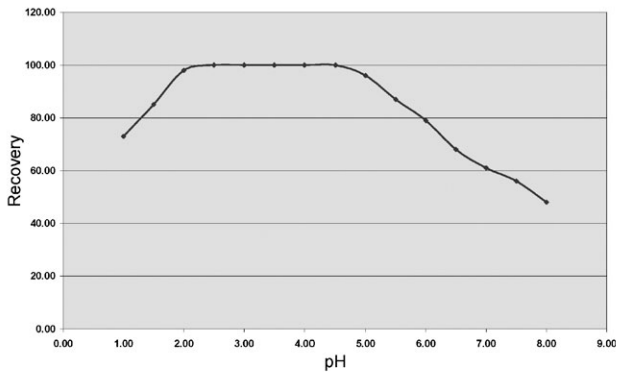


Fig. 1 Effect of pH of sample solution on recovery of Fe^{3+} ion.

Table 2 Separation of iron from binary mixtures[a]

Diverse ion	Amount taken/mg	Found (%)[c]	Recovery of Fe^{3+} ion (%)[c]
Ni^{2+}	2.5	7.0 (0.5)	99.5 (0.5)
K^{+}	6.5	NADP[b]	100.1 (0.5)
Na^{+}	6.5	NADP	100.1 (0.4)
Cd^{2+}	3.4	NADP	99.7 (0.6)
Co^{2+}	5.0	56.0 (0.8)	95.0 (1.0)
Zn^{2+}	4.3	12.0 (0.4)	100.0 (0.8)
Mn^{2+}	2.5	NADP	100.0 (0.6)
Mg^{2+}	2.5	NADP	99.6 (1.2)
Ca^{2+}	5.2	NADP	99.4 (2.1)
Cu^{2+}	2.6	10.0 (2)	99.1 (1.3)
Hg^{2+}	10.0	5.0 (1.2)	91.7 (1.1)
Hg_2^{2+}	10.0	3.0 (0.5)	92.8 (1.2)

[a] Initial samples contained 2.5 μg Fe^{3+} and different amounts of divers ions in 50 ml of water. [b] No adsorption passes through column. [c] Values in parentheses are RSDs based on four replicate analyses.

Effect of pH and flow rates on the adsorption of Fe^{3+} ions

The pH is a very important factor in the separation of metal ions by chelation, because it will determine the values of the conditional stability constants of the metal complexes on the surface of the sorbent. Owing to the presence of a hydroxyl group on the ligand L structure, it is expected that the extent of its complexation will be sensitive to pH. Thus, the influence of the pH of an aqueous sample on the recovery of 2.5 μg of Fe^{3+} from 50 ml of solution was studied in the pH range 1–8. The pH was adjusted by using 0.01 M of either nitric acid or sodium hydroxide solutions. The results are shown in Fig. 1. As can be seen, the recovery of Fe^{3+} ion increases with increasing pH of the solution until a pH of about 2.5 is reached. Maximum and constant retention of Fe^{3+} ions by the modified column was obtained in the pH range 2.5–4.5. Therefore, the pH was adjusted with 0.01 M HNO_3 to about 3.5 for subsequent experiments. With pH values higher than 4.5, there is a possibility of the hydrolysis of iron ions in the solution. The effect of the flow rates of the sample and stripping solutions on the retention and recovery of Fe^{3+} ions was investigated. It was found that retention of the Fe^{3+} ions was independent of flow rate from 0.5–1 ml min^{-1}.

Quantitative stripping of Fe^{3+} ions from the column achieved in a flow rate of 0.5–2 ml min^{-1}, using 2 × 5 ml of 0.1 M EDTA as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of Fe^{3+} ions. Thus, subsequent experiments were carried out with a flow rate of about 1 ml min^{-1}.

Analytical performance

The measurement of breakthrough volume is important in solid-phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without

Table 3 Determination of iron in water samples

Sample	Fe added/ μg L^{-1}	Found by this method/μg L^{-1}	Recovery (%)[a]
River water	0	33.0	—
	5.0	38.7	101.8 (0.4)
	10.0	42.8	99.5 (0.5)
Kerman drinking water	0	22.0	—
	5.0	27.2	100.7 (0.8)
	10.0	31.9	99.7 (0.6)

[a] Values in parentheses are RSDs based on five replicate analyses.

Table 4 Comparison with other systems[a]

Parameter	FAAS this method	FAAS[24]	FAAS[25]	FAAS[26]	FAAS[27]	FIA[28]	FIA[29]
Detection technique	SPE-FAAS	SPE-FAAS	SPE-FAAS	SPE-FAAS	SPE-FAAS	SPE-CL	ICP-MS
Sorbent	Analcime Zeolit modifid with ligand (L)	Pyrrolidine dithiocarbamate on a column (Chromosorb-102)	Cellulose loaded with 8-hydroxyquinoline	Naphthalene tetraoctylammonium bromide	SiAT	Amberlite XAD-4-HEED	PTFE knotted reactor
Eluent	EDTA (0.1 M)	Acetone	HCl (1 M)	HNO_3 (1.5 M)	HCl (1 M)	HCl (0.75 M)	HNO_3 (1 M)
Sample flow-rate/ml min^{-1}	1	3.5	3	2	1.5	2.8	5
Elution flow-rate/ml min^{-1}	1	—	2	—	—	1	1.1
Detection limit/ng ml^{-1}	0.084	11	3.3	12	3	0.096	0.08
Working range/ng ml^{-1}	1–300	NR	NR	25–350	NR	0.256–61.6	0.2–120
Repeatability (%)	1.13	5	3.94	1.8	1.5	<4	2.9
Preconcentration factor	60	60	300	36	NR	NR	—
pH	3.5	4–6	>3	3	—	3.3	—
Recovery (%)	~99	>95	98	>99	98	—	95–103

[a] FIA: flow-injection analysis; ICP-MS: inductively coupled plasma-mass spectrometry; CL: chemiluminiscence; SiAT: silica gel modified with 2-aminotiazole groups; HEED: *N*-hydroxyethylethylenediamine; PTFE: polytetrafluoroethylene; NR: not reported.

loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 2.5 μg of Fe^{3+} in 100, 200, 300, 400, 500 and 600 ml of water and the recommended procedure was followed. In all cases, the extraction by column was found to be quantitative. Thus, the breakthrough volume for the method should be greater than 600 ml.

The limit of detection (LOD) of the proposed method for the determination of Fe^{3+} was studied under the optimal experimental conditions. The LOD obtained from $C_{LOD} = K_b S_b/m$[23] for a numerical factor $K_b = 3$ is 84 ng per 1000 ml. The reproducibility of the proposed method for the extraction and determination of 2.5 μg of Fe^{3+} from 50 ml of water was also studied. The results obtained for 10 replicate measurements revealed a RSD of 11.3 ppt.

In order to investigate the selective separation and determination of Fe^{3+} ion from its binary mixtures with various metal ions, an aliquot of aqueous solution (50 ml) containing 2.5 μg of Fe^{3+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 2. They clearly indicate that Fe^{3+} ions in the binary mixtures are retained almost completely by the column, while retention of other cations by the column is very low and they can be separated from Fe^{3+} ions.

In order to assess the applicability of the method to real samples, it was applied to the separation and recovery of iron(III) ions from different waters, and the results are summarized in Table 3. As is obvious, the Fe^{3+} ions added can be quantitatively recovered from the water samples.

Comparison of this method with other systems

Several methods have been reported in the literature for the preconcentration and determination of iron. As can be seen in Table 4, the main advantages of this method are: (i) natural Analcime is very cheap, (ii) the preparation of the extraction system is simple and fast, (iii) a good preconcentration factor can be achieved and (iv) the detection limit and working range of the present work are very good. Therefore, this method was successfully applied to the determination of iron in water samples with excellent recoveries.

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