Preconcentration and Separation of Iron and Cobalt Using Solid Phase Extraction and Their Determination by Flame Atomic Absorption Spectrometry

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The adsorptive potential of barium-strontium titanate based on glass fiber filter (BBST) for iron and cobalt ions were investigated and the conditions of adsorption and elution were studied. A solid phase extraction method has been developed to separate and concentrate trace amounts of iron and cobalt ions from aqueous samples for the measurement by flame atomic absorption spectrometry. By the passage of aqueous samples through barium-strontium titanate based on glass fiber filter, iron and cobalt ions adsorb quantitatively. The results showed that the barium-strontium titanate based on glass fiber filter had adsorption capacity towards the iron and cobalt ions when the pH value was not less than 4. The adsorption capacities of barium-strontium titanate based on glass fiber filter for iron and cobalt ions were found to be 15.29 mg/g and 5.02 mg/L, respectively. The iron and cobalt ions could be completely eluted by 0.5 g/L EDTA. The iron and cobalt were concentrated successfully and the pre-concentration factors were all not less than 100. A new method for determination of trace iron and cobalt in water based on barium-strontium titanate based on glass fiber filter and flame atomic absorption spectrometry determination was proposed. The detection limits of this method for iron and cobalt were 0.06 µg/L and 0.05 µg/L, respectively. The method has been applied to the determination of trace iron and cobalt ions in tap, lake and river water samples with successfully results.

Key Words: Solid phase extraction, Preconcentration, Iron, Cobalt, Barium-strontium titanate, Flame atomic absorption spectrometry.

INTRODUCTION

As we all known, that iron and cobalt are all essential elements for the functioning of many vital processes. The determination of iron and cobalt at trace levels in environmental is one of the targets of analytical chemists, due to their important roles in our life[1-3]. At present, the determination method of iron and cobalt in water mainly includes spectrophotometry, atomic absorption method and inductively-coupled plasma spectrometry, *etc.*[4]. However, for the lead with low content, it is hard for direct determination using these methods without pre-separation and enrichment. The common separation and enrichment methods are liquid-liquid extraction, coprecipitation, cloud point extraction and solid-phase extraction, *etc.*[5-8]. Of all preconcentration and separation procedures solid-phase extraction several advantages: large preconcentration factors that can be obtained in a short time, simplicity of phase separation and suitability for automation[9,10]. Various solid phase extraction materials including Diaion HP-20[11], cellulose[12], activated carbon[13], Lewatit S 100[14], SDS coated alumina[15] polyurethane foam[16], Chelex 100[17], microcrystalline naphthalene[18], modified silica[19] and diaion HP-2MG[20]. With the development of nanosecond science and technology in recent years, nano-

powder adsorption agents have been successfully used in separation and enrichment[21-23]. We had used barium-strontium titanate based on glass fiber filter (BBST) in the adsorption of heavy metals in water[24]. However, using BBST as solid phase extraction agent for preconcentration of iron and cobalt has not been studied. In this paper, barium-strontium titanate based on glass fiber filter (BBST) was applied to the adsorption of iron and cobalt in water. In addition, the optimal adsorption and desorption conditions were obtained. This agent was used in the enrichment and determination of iron and cobalt ions in tap, lake and river water samples.

EXPERIMENTAL

A WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co. Ltd.), equipped with hollow cathode lamps for iron and cobalt. The operation conditions are summarized in Table-1.

All pH measurements were made with a PHS-3C model digital pH meter (Shanghai REX Instrument Factory, Shanghai, China) equipped with a combined pH electrode. A constant temperature bath shaker (Jintan Experiment Instrument Factory, Jiangsu China) was used to shaking for adsorption and elution.

TABLE-1
FURNACE ATOMIC ABSORPTION SPECTROMETRY
OPERATING CONDITIONS

Element	Wave length (nm)	Spectral band width (nm)	Lamp current (mA)	Burne heigh (mm)	Acetylene gas consumption (mL/min)
Fe	248.3	0.2	12.0	9.0	2200
Co	240.7	0.2	7.0	5.0	4500

A barium-strontium titanate based on glass fiber filter (BBST) was prepared in our laboratory as described[24].

Standard stock solutions of iron and cobalt: 0.1 g/L, prepared with spectrum pure iron and cobalt metal (Sinopharm Chemical Reagent Co., Ltd, China) using conventional method and diluted to the required concentration when use, respectively. Nitric acid and sodium hydroxide (all come from Sinopharm Chemical Reagent Co., Ltd, China) were used to adjust pH of the sample solutions. The water in this study was distilled water. All the chemicals were analytical reagent grade.

Static adsorption experiment: A certain amount of iron or/and cobalt was sampled into 50 mL colourimetric cylinder with plug and mark (calibrated). The pH was adjusted to 4. After diluting to the mark with water, 0.1 g of BBST was added. Cover the plug and shake the cylinder for 0.5 h. The supernatant fluid was directly measured under the selected instrument working conditions by atomic absorption method. The content of iron or/and cobalt was determined and the absorption capacity was calculated.

Elution experiment: The absorption agent was eluted with water for twice. 5 mL of elution agent was shaken for 5 min and then directly sampled to atomic absorption spectrophotometer. The content of iron or/and cobalt was determined.

RESULTS AND DISCUSSION

Effect of pH: 10 mg of iron and 0.5 mg of cobalt were sampled to 50 mL colourimetric cylinder. After adjusting the pH to required value, the solutions were diluted to 50 mL with water at corresponding pH. The adsorption capacities of BBST to iron and cobalt were measured according to the experimental method. The results showed that the adsorption capacity of BBST to iron and cobalt were all high. However, they were greatly affected by pH. The increasing pH resulted in the increase of adsorption capacity. The adsorption of iron at the pH range of 3 to 8 and of cobalt at the pH range of 4 to 8, were over 95 % (Fig. 1). To preconcentrate iron and cobalt simultaneously and to avoid the precipitation of metal ions at high concentration, pH 4 was selected as the optimal pH condition in this study.

Effect of oscillation period: At room temperature, the adsorption capacities were determined with different oscillation periods (Fig. 2). The results indicated that the adsorption capacity increased with the increase of oscillation period and they all reached equilibrium at 0.5 h. Therefore, the oscillation period was 0.5 h in this study.

Elution conditions: After adsorbing under optimal adsorption conditions, 5 mL of HNO_3 (0.05 mol/L-2.5 mol/L) or EDTA (0.25 g/L-2.5 g/L) was used for elution liquid for 5 min, respectively, to determine the recovery. The results showed that the recovery increased with the increase of EDTA

concentration. When the concentration of EDTA was higher than 0.4 g/L, the recovery was up to 99 %. On the other hand, the recoveries were all lower than 95 % when HNO_3 was used as the elution liquid. Therefore, 0.5 g/L of EDTA was used in present study. After eluting, the BBST was dried for reusage for 10 times. The adsorption capacity did not decrease, indicating that this adsorption agent having strong stability.
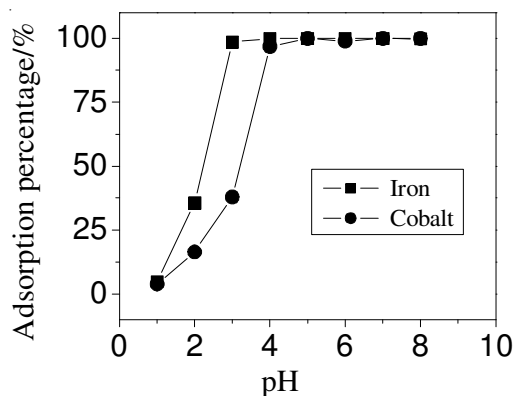

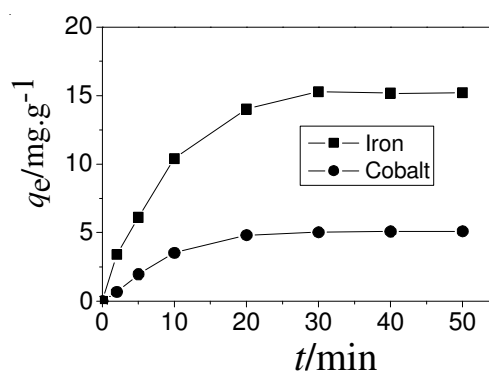Fig. 1. Effect of pH on the adsorptions

Fig. 2. Effect of contact time on iron and cobalt adsorption

Static adsorption capacity: According to the Fig. 2, under the optimized adsorption conditions, the static adsorption capacity of BBST to iron and cobalt were 15.29 mg/g and 5.02 mg/L, respectively. The adsorption capacities of BBST to iron and cobalt were large and the recoveries were convenient. Therefore, recovery was an ideal block enrichment material for iron and cobalt.

Enrichment factor and detection limit: In order to explore the possibility of enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention of iron and cobalt was also investigated. For this purpose, 20 µg of Fe and 5 µg of Co were dissolved together in various volumes of water. After adsorbing and eluted with 5 mL of elution liquid, the recoveries were calculated as listed in Table-2.

It could be seen that when the solution volume was 500 mL, the recoveries were above 95 % under the selected enrichment conditions. The enrichment factors were all not less than 100. The detection limits were calculated using the concentration of three times standard deviation, calculated from 11 runs of the blank solution with concentrations of iron and cobalt ions at 0.06 µg/L and 0.05 µg/L, respectively.

TABLE-2
PRECONCENTRATION AND RECOVERIES
OF IRON AND COBALT IONS

Volume of the solution (mL)	The quantity in eluent (µg)		Recovery (%)		Enrichment factor
	Fe	Co	Fe	Co	
50	20.25	4.97	101.2	99.4	10
100	19.33	5.03	96.6	100.6	20
150	19.26	4.94	96.3	98.8	30
200	19.98	4.88	99.9	97.6	40
250	19.02	4.83	95.1	96.6	50
500	19.00	4.81	95.0	96.2	100

Effect of coexisting ions: Various interference ions were added into 50 mL colourimetric cylinder containing 20 µg of iron and 5 µg of cobalt. The recoveries of iron and cobalt were determined according to experimental method by controlling the error within ±5 %. The results showed that 2000-fold of Na^+, K^+, NH_4^+, NO_3^-, 1000-fold of PO_4^{3-}, Cr(VI), Cl^-, Ca^{2+}, Mg^{2+}, 500-fold of Cr(III), Ag^+, Cd^{2+}, 100-fold of Zn^{2+}, Pb^{3+}, Al^3 and 50-fold of Ni^{2+}, Cu^{2+} did not interfere with the determination.

Analysis of sample: The lake water (Nan-hu Lake, Shenyang, China) and river water (Hun-he River, Shenyang, China) samples were filtered with 0.45 µm filter membrane, respectively and the tap water (collected from the water supply of Shenyang city) was sampled directly. After adjusting the pH, the water samples were enriched and adsorbed according to the experimental method and then determined with flame atomic absorption spectrometer. Meanwhile, the recovery testes were also conducted. The results were compared with those obtained by graphite furnace atomic absorption spectrometry (GFAAS), as listed in Table-3. The recoveries were in the range of 93.0 %-103.5 % and the determination results were in good agreement with those obtained by graphite furnace atomic absorption spectrometry.

TABLE-3
DETERMINATION OF IRON AND COBALT
IONS IN WATER SAMPLES (n = 6)

Samples of water	Added (µg/L)		Found (µg/L)		Recovery (%)		Found by GFAAS (µg/L)	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Tap water	0	0	21.4	1.87	-	-	22.15	1.94
	50	2	70.2	3.73	97.6	93.0	-	-
	100	5	119.5	6.89	98.1	100.4	-	-
Lake water	0	0	151.0	26.35	-	-	150.66	25.37
	100	20	246.1	46.15	95.1	99.0	-	-
	200	50	348.9	74.73	98.9	96.8	-	-
River water	0	0	96.5	8.31	-	-	96.21	8.41
	50	10	145.6	18.66	98.2	103.5	-	-
	100	20	191.9	27.9	95.4	97.9	-	-

Conclusion

According to the research results in this paper, it could be concluded that the barium-strontium titanate based on glass fiber filter (BBST) had adsorption capacity towards the iron and cobalt when the pH value was not less than 4. The adsorption capacities of BBST for iron and cobalt were found to be 15.29 mg/g and 5.02 mg/L, respectively. The iron and cobalt could be completely eluted by 0.5 g/L EDTA. The iron and cobalt were concentrated successfully and the pre-concentration factors were all not less than 100. A new method for determination of trace iron and cobalt in water based on BBST and flame atomic absorption spectrometry determination was proposed. The detection limits of this method for iron and cobalt were 0.06 µg/L and 0.05 µg/L, respectively. The method has been applied to the determination of trace iron and cobalt in tap, lake and river water samples, the recoveries were all 93.0-103.5 % and the results were found to be agreement with those by graphite furnace atomic absorption spectrometry.

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