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Application of a new water-soluble polyethylenimine polymer sorbent for simultaneous separation and preconcentration of trace amounts of copper and cobalt and their determination by atomic absorption spectrophotometry

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ABSTRACT

In this work, a water-soluble polymer, polyethylenimine (PEI) was used for the simultaneous separation and preconcentration of trace Cu and Co prior to their determination by flame atomic absorption spectrometry. For this purpose, the sample and the PEI solution were mixed and the metal-bound polymer was precipitated by adding acetone. The precipitate was separated and dissolved in a minimum amount of water and aspirated into a flame AAS. By increasing the ratio of the volumes of sample to water used in dissolving the precipitate, the analyte elements were concentrated as needed. The sorption is quantitative in the pH ≥ 6 . Detection limits were 5.6 $\mu\text{g/L}$ for Cu and 5.8 $\mu\text{g/L}$ for Co. This method is simple, fast and precise. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Polyethylenimine polymer sorbent;
Simultaneous separation and preconcentration;
Copper and cobalt;
Atomic absorption spectroscopy.

INTRODUCTION

Cobalt is an essential micronutrient for life. Determination of low levels of cobalt by flame atomic absorption spectrometry (FAAS) often demands separation and preconcentration steps because of insufficient sensitivity or matrix interference. Several procedures of enrichment have been developed for cobalt determination involving different analytical techniques, such as coprecipitation^[1], or liquid-liquid^[2], cloud point^[3] or solid-phase^[4,44-46] extraction. Processes involving solid-phase extraction^[5] show several advantages, like availability and easy recovery of sorbent, attainability of high preconcentration factors, and facility of handling. Therefore, these procedures avoid or minimize the use of organic solvents that are generally toxic.

Online preconcentration systems using solid-phase

extraction are opportune for metal determination, due to their flexibility, simplicity, high sample throughput and versatility. These characteristics permit the use of online systems coupled with different detectors. Many online procedures using solid-phase extraction can be found in the literature. The materials generally used are ion-exchangers^[6,7], silica^[8,9], activated alumina^[10,11], carbon^[12], fullerene^[13], polyurethane foam^[14,15] and chelating resins^[16].

The most common techniques available for preconcentration of metal ions from aqueous samples are solvent extraction and solid-phase extraction using various adsorbents such as activated carbon^[17], cellulose^[18], microcrystalline naphthalene^[19-21], amberlite XAD resins^[22], octadecylsilica membrane disk^[23], synthetic zeolites^[24], analcime zeolites^[25], silica^[26] and other numerous materials. These solid water-insoluble materials

should meet the following requirements as far as possible to be successfully applied in batch or column techniques for the preconcentration and separation of trace elements: the materials should have large surface area and uniform particle size, it should not swell and the analytes should be collected and eluted with minimum experimental procedure fast and quantitatively. Blank values should be low and adsorption capacity should be large enough not to be overloaded with matrix constituents. The different methods for the separation and preconcentration of copper and cobalt have been reported. A flame atomic absorption spectrophotometer (FAAS) has been widely used for the determination of copper and Cobalt^[27-30] because of its high specificity, while not being an expensive instrument. Other techniques including electrothermal atomic absorption spectrometry^[31-34] due to its further sensitivity and inductively coupled plasma^[35,36] have also been applied.

A few papers have reported about water-soluble polymer for preconcentration and separation of trace elements by precipitating to a solvent such as acetone. Water-soluble polymers such as polyacrylic acid for preconcentration and separation of Cd, Cu and Zn^[37], polyvinylpyrrolidinone (PVP) for Pb, Cu and Co^[38] and polyacrylamide for the preconcentration and separation of Cr, Pb and Cu^[39] have been used. In these methods, sample and polymer solution were mixed and the analyte-bound polymer was precipitated in excess acetone. Analyte is completely and very fast bound to polymer. The precipitate was separated and dissolved in water and analyzed by FAAS. The procedure is simple, fast and free of interference.

Polyethylenimine (PEI) is well known for its metal chelation potentialities^[40,41]. Interactions of metal ions with watersoluble polymers such as polyethylenimine are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase. The features of coordination between polymer and metal ions may be described by the usual coordination theories, but some special aspects may be considered. When intra-chain complexes are predominant, it is normally recognized the existence of a polymer domain with near constant concentration of ligands, since the distances between them keep in a narrow range for a given polymer chain, this is respon-

sible for that the chelating reaction appears as a onestep reaction^[42]. The reaction between the polymeric agent (PEI), the proton (H⁺) and the metal cation (Cu²⁺) is represented by the following equilibrium equations^[43]:



To date no paper has reported the use of PEI for the separation and preconcentration by precipitating to a solvent such as acetone.

The aim of this work is to investigate the use of PEI for simultaneous separation and preconcentration of copper and cobalt by precipitating to acetone prior to their determination by FAAS.

EXPERIMENTAL

Apparatus and reagents

A Varian model spectrAA 220 atomic absorption spectrometer was used for measuring Cu(II) and Co(II) in air-acetylene flame. Instrumental parameters were adjusted according to manufacture's recommendations (TABLE 1). A Metrohm 713 pH meter was employed for pH measurements. A Damon model centrifuge equipped to timer and speed control was employed for centrifuging of samples. All reagents were of analytical reagent grade. The stock solution of copper(II) was prepared by dissolving 0.2500g of copper powder 99.9995% (Aldrich) in a minimum volume of 1:1 nitric acid with heating, the solution was boiled to expel brown fumes, cooled and diluted with distilled water to 250.0 mL. The standard working solutions were diluted daily prior to use. The stock solution of Cobalt(II) was prepared by dissolving 1.5380g CoSO₄·H₂O 99.99% (Merck) in distilled water and diluted to 500.0 mL. A 20% solution of polyethylenimine (PEI, molecular weight: 600,000-10,00,000) (Fluka) was prepared in distilled water. A saturated solution of potassium nitrate was prepared by dissolving KNO₃ (Aldrich) in distilled water.

TABLE 1 : Instrumental settings

Cu	Co	Element
324.7	279.5	Wavelengths (nm)
4	5	Current lamp (mA)
0.5	0.2	Slit width (nm)
1.5	1.5	Acetylene flow (L/min)
3.5	3.5	Air flow (L/min)

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General procedure

An aliquot of copper(0.25-30.0 μ g) and cobalt (0.15-20.0 μ g) was taken in a 50mL centrifuge tube. After adding 1mL of saturated KNO_3 and 0.5mL of polymer solution(20%), pH was adjusted to 7-8 with HNO_3 . The solution was diluted to 10mL with deionized water. Then, the metal bound polymer was precipitated by adding 30mL acetone to the sample solution, immediately. In order to speed up the precipitation, the tube content was centrifuged. The supernatant was separated simply by decantation. The precipitate was dissolved in 5.0mL of distilled water and aspirated directly into the flame of AAS against the blank prepared in the same manner without the addition of metal ions.

RESULTS AND DISCUSSION

Reaction conditions

Reaction conditions were established with the use of 5.0 μ g Cu(II) and 5.0 μ g of Co(II). Adsorptions were carried out at different pH, keeping other variables constant. It was found that copper and cobalt were quantitatively adsorbed in $\text{pH} \geq 6$. The pH curves for both elements are shown in figure 1. Under pH 6, a majority of amine sites are protonated and can not take part in the chelation process, but above pH 6, a portion of amino groups is in a neutral form, leading to a donor-acceptor interaction with metal ions. In the subsequent studies pH was maintained at 7-8(Figure 1). Adding saturated KNO_3 solution to the sample, by salting out effect, causes that the precipitation is completed faster with less amount of acetone, and the precipitate is been bulky and easy to separate. Various salts were tested and KNO_3 was selected due to it's high solubility in water and the absence of interferences. The amount of KNO_3 was optimized and amount of one milliliter was used in all experiments. The volume of the first aqueous phase was varied in the range 3-60mL under the optimum conditions. By adding KNO_3 and further amounts of acetone, can be extract analytes from the first solution, but was used from 10.0mL of the first aqueous phase, because the treating with large volumes is difficult. The volume of water for dissolving of the precipitate was tested. For further the sensitivity and the

preconcentration factor of the method, 5.0mL of distilled water was used in the present work. The necessary volume for the precipitating depends on the first aqueous phase. Large volumes of the sample need further acetone. Therefore 10mL of the first aqueous phase and 30mL acetone was used. Different amounts of polymer were added to the sample solution while keeping other variable constant. It was observed that in the large amounts of polymer, the final solution (after dissolving of precipitate in water) has a high viscosity, hence, aspiration and absorbance decreased, therefore 0.5mL of polymer (20%) was the best amount and was used in subsequent studies.

Sorption capacity of polymer

The maximum sorption capacity of the polymer using excessive analyte concentrations was 13mg Cu/g polymer. This is considerably higher than water-insoluble polymer, therefore a small amount of polymer was enough to collect all the metal ions from samples. 0.5mL PEI 20% was used in all experiments.

The rate of procedure

The complexation between polymer and metal ions was very fast, and the reaction was readily completed. In addition, the precipitate dissolved in water immediately. The rate determining step of the complete method was the precipitating that was further speed up with aid of saturated KNO_3 solution and centrifuging, but when water-insoluble materials are used, both sorption and elution are time-consuming and influence the total duration of the method.

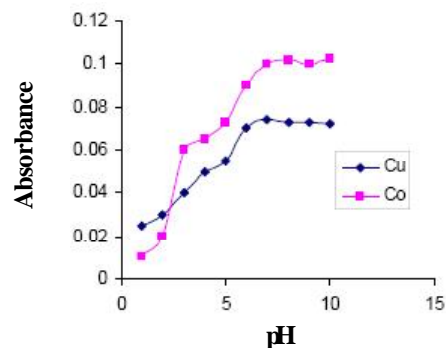


Figure 1 : Effect of pH on adsorption of Cu and Co. Conditions: 5.0 μ g Cu and 5.0 μ gMn; 0.5mL polymer; 1mL KNO_3 ; 30mL acetone; instrumental settings were same as TABLE 1

Calibration and sensitivity

Calibration curves for the determination of copper and cobalt was prepared according to the general procedure under the optimum conditions. The linearity for copper in the final solution was maintained in the concentration range of 0.05-6 $\mu\text{g}/\text{mL}$ and for cobalt 0.03-4 μmL (Figure 2). The calibration curve equation for copper $A=0.070c(\text{ppm})+3.11\times 10^{-2}$ with correlation factor 0.9882 and for cobalt $A=0.0764c(\text{ppm})+0.0936$ with correlation factor 0.9979 is obtained. The sensitivity for 1% adsorption was 6.8 $\mu\text{g}/\text{L}$ for cobalt and 61 $\mu\text{g}/\text{L}$ for copper. Eight replicate determination of 5.0 μg copper in final 5.0mL water solution gave a relative standard deviation of $\pm 2.3\%$ for cobalt and $\pm 2.6\%$ for copper. The detection limits were calculated 5.6 $\mu\text{g}/\text{L}$ for Cu and 5.8 $\mu\text{g}/\text{L}$ for Co.

Effect of diverse ions

Various salts and metal ions were added to a solution containing 5.0 μg of Cu(II) and Co(II) ions and the general procedure was applied. The tolerance limit (error < 3%) is given in TABLE 2. Among the metal ions studied, most did not interfere even at the g-mg level. Among the metal ions studied, most did not interfere even at the mg level. Thus the method is highly selective and may safely be applied for the determination of Cobalt and copper in various environmental and biological samples.

Analysis of copper and cobalt in standard alloys

The accuracy of the proposed method has been tested for the determination of copper and cobalt in standard reference alloys: NKK, no: 1021 alloy; NKK, no: 920 alloy and JSS, stainless steel no: 651-7 alloy. A 0.1000 g alloy was taken in a beaker and dissolved in concentrated nitric acid ($\mu 10\text{mL}$) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100.0mL with distilled water in a calibration flask. An aliquot of the pre-treated sample solution was taken and analyzed by the general procedure. The results are given in TABLE 3 which are in good agreement with the certified values.

Analysis of copper and cobalt in real samples

The applicability of the proposed method was evaluated with real samples. Copper and cobalt were deter-

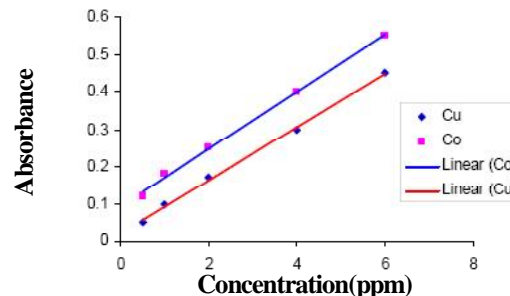


Figure 2 : Calibration curves for Cu and Co. Conditions and instrumental settings were same as figure 1

TABLE 2 : Effect of different salts and metal ions

Tolerance limit(mg)		Salt or metal ion
Co	Cu	
1000	700	NaHCO ₃
500	500	KH ₂ PO ₄
500	500	K ₃ PO ₄
400	500	K ₂ S ₂ O ₈ , Na ₂ C ₂ O ₄
400	400	NaF
200	500	Sodium potassium tartarate
200	400	Na ₂ S
450	400	KBrO ₃
250	300	NaClO ₄
450	250	KSCN
200	250	Trisodium citrate
400	150	NH ₄ Cl
150	250	Disodium-EDTA
50	40	NaBiO ₃
50	50	Al(III)
50	50	Au(III)
50	50	Hg(II), Pb(II), Mo(VI)
40	50	Tl(I)
40	40	Cd(II)
40	35	Zn(II)
30	40	Sn(II)
35	30	Ce(III)
-	50	Co(II)
50	-	Cu(II)
20	35	Cr(III)
20	20	Co(II)
25	25	Mg(II)
15	5	Ni(II)
10	8	Fe(III)
7	5	Ag(I)

Conditions: 5.0 μg Cu and 5.0 μg Co; 0.5mL polymer; pH: 7-8; 1mL KNO₃; 30mL acetone

mined in biological samples. A 0.50g sample of the plant samples(Beet and Kadoo) was taken separately in a beaker and dissolved in concentrated nitric acid and perchloric acid(3:1) by heating on a hot plate. The solution was cooled, diluted and filtered if needed. The filtered was made to 50.0mL with distilled water in a calibration flask. An aliquot of the sample solution was

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TABLE 3 : Analysis of copper and cobalt in standard alloys

Recovery (%)	Founda (%)	Composition (%)	Sample
98.0	Co: 0.196±0.008	Si: 5.56, Zr: 0.01, Cu: 2.72, Ca: 0.004, Mg: 0.79, Fe: 0.99, Ni: 0.14, Co: 0.20, Sn: 0.10, Cr: 0.03, Bi: 0.01, Zn: 1.76, Ti: 0.04, Pb: 0.18	NKK, no. 1021: Al, Si, Cu, Zn alloy
99.2	Cu: 2.70±0.06		
95.5	Co: 0.191±0.007	Si: 0.78, Ni: 0.29, Fe: 0.72, Zn: 0.80, Cu: 0.71, Ti: 0.15, Co: 0.20, Sn: 0.20, Mg: 0.46, Pb: 0.10, Cr: 0.27, V: 0.15, Co: 0.10, Bi: 0.06, Sb: 0.01, Ga: 0.05; Ca: 0.03	NKK, no. 920: aluminum alloy
102.8	Cu: 0.73±0.03		
99.4	Co: 1.71±0.09	C: 0.047, Co: 1.72, S: 0.0063, Cr: 18.60, Cu: 0.082, Al: 0.002, Si: 0.72, P: 0.028, Ni: 9.20, Mo: 0.084, Co: 0.22, N: 0.0249	JSS, no. 651-7: stainless steel
101.2	Cu: 0.083±0.004		

NKK, Nippon Keikinzo Kogyo; JSS, Japanese standards of iron and steel. conditions: 0.5mL polymer 20% ; pH: 7-8 ; 1mL KNO₃; 30mL acetone. ^aAverage of three determination, ±S.D.

TABLE 4 : Determination of Cu and Co in real samples

Recovery (%)	FAAS (µg/g)	Recommended procedure (µg/g) ^a	Element determined	Sample
98.4	1.73±0.07	1.68± 0.08	Co	Human hair
100.1	11.45±0.06	11.50±0.05	Cu	(male)
99.3	76.3±0.4	75.5±0.4	Co	Beet
100.2	6.24±0.06	6.30±0.05	Cu	
97.3	22.3±0.6	21.8±0.6	Co	Kadoo
99.7	9.52±0.07	9.48±0.07	Cu	
97.5	0.213±0.008	0.210±0.004 ^b	Co	Apple juice ^c
97.6	0.64±0.05	0.66±0.02 ^b	Cu	

Conditions: 0.5mL polymer (20%); 1mL KNO₃; pH: 7-8; 30mL acetone. ^aAverage of three determination, ±S.D. ^bµg/mL. ^cFrom Annanab company (Tabriz, Iran).

taken individually and copper and cobalt were determined by the general procedure. The results obtained are given in TABLE 4. A 4.20g sample of human hair was washed by acetone and burned in furnace at 700°C until a white powder was obtained. The obtained ash was dissolved in a minimum volume of concentrated

nitric acid with heating. The solution was boiled to expel brown fumes, cooled and diluted with distilled water to 20.0mL in a calibration flask. An aliquot of sample solution was taken individually and cobalt and copper were determined by the general procedure. The results were summarized in TABLE 4.

CONCLUSION

Water-soluble polymer, polyethylenimine could be successfully applied for simultaneous separation and preconcentration of copper and cobalt. The method offered is simple, fast and precise and can reliably be applied for the analysis of many real samples containing complex matrix. The success of the method depends on precipitation and dissolution process. The disadvantage of the method is the consumption of much acetone, but it could be distilled and re-used several times. The concentration factor is limited due to the need of excess acetone for completed precipitation.

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