Cobalt separation from water and food samples based on penicillamine ionic liquid and dispersive liquid-liquid microextraction before determination by AT-FAAS

Yaghoub Pourshojaei [a,*] and Alireza Nasiri [b]

[a] *Department of Medicinal Chemistry, Faculty of Pharmacy, Kerman University of Medical Sciences, Kerman, Iran.*
[b] *Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Postal code:7619813159, Kerman, Iran*

ABSTRACT

The cobalt compounds have adverse health effect on human and caused to damage of the DNA cells, neurological and endocrine systems. Therefore, the separation and determination of cobalt in water and food samples must be considered. In this research, the (2S)-2-amino-3-methyl-3-sulfanylbutanoic acid (penicillamine) as a chelating agent mixed with ionic liquid (OMIM PF_6) /acetone and used for extraction of cobalt from 50 mL of water samples by ultra-assisted dispersive liquid-liquid microextraction (USA-DLLME) at pH=6. Based on procedure, the samples were shaked for 5 min (25°C) and after complexation of cobalt ions by thiol and amine group of penicillamine, the ionic liquid phase separated in the bottom of the conical tube by centrifuging for 3.0 min. The upper liquid phase was vacuumed by the auto-sampler and the Co^{2+} ions back extracted from the ionic liquid/ penicillamine in acidic pH. Finally, the cobalt concentration in remained solution was determined by atom trap flame atomic absorption spectrometry (AT-FAAS). The main parameters such as the sample volume, the penicillamine amount, the ionic liquid amount and the shaking time were optimized. The linear range, the detection limit (LOD) and enrichment factor were obtained 1.5-62 μg L^{-1}, 0.38 μg L^{-1} and 98.5, respectively (r = 0.9995, RSD%=2.2). The procedure was validated by ET-AAS analysis.

1. Introduction

Cobalt compounds exist in two valence forms include cobalt (Co II, cobaltous, Co^{2+} and Co III, cobaltic, Co^{3+}), the other forms have not environmentally available. Also, the other cobalt compounds have toxic effect in the environment and the human body by extra exposure [1]. The people is exposed to cobalt through inhalation of air and food and drinking water. Cobalt ions enter to environment from numerous industrial factories such as heavy metals activity process, the grinding, the mining and paint [2]. Furthermore, it can be used for a medical process for the medicine Company. The cobalt compounds are widely dispersed in air with a low concentration less than 2.0 ng m^{-3} [3, 4]. Cobalt has a low concentration range between 0.1-5 μg L^{-1} in drinking water. The cobalt concentration in river, the groundwater, the ocean water has an average value about 0.3 μgL^{-1} [5]. Feng et al reported the concentrations of cobalt in the groundwater had lower than 0.01 mg L^{-1} which is lower than other heavy metals [6]. Lim *et al* showed an applied model for the heavy metals such cobalt in

wastewater based on fly ash near landfills [7]. United States Environmental Protection Agency (EPA) reported that the cobalt levels in sediment and surface water were 80 µg g^{-1} and 86 µg L^{-1}, , respectively [2]. Food analysis in dietary cobalt intake such as vegetables, cereals and fish is very important way to control cobalt toxicity in human body which is especially significant in children [8]. Besides, the skin contact is a main way that cobalt was entered to human body. Cobalt as an essential metal exists in the human body and the maximum amount of it generally concentrated in the liver. Cobalt in eggs has biological role in vitamin B12 and named cyanocobalamin [9]. It uses in structure of vitamin B$_{12}$ and produce the red blood cells in bones and define from anemia in body [9]. Cobalt toxicity cause several health problems such as cardiomyopathy, nerve/thyroid problems, hearing and visual impairment, neuropathy, tinnitus and glomerulonephritis [10, 11]. Therefore, the accurate results for determination of cobalt must be considered by a new technology. The normal concentration of cobalt is equal to 1.0 ng mL^{-1} for environmental or occupational exposure and more than this value cause to toxicity. The sources of cobalt can be entering to human body from occupational/environmental/food exposures. The blood Co concentration is 100 µgL^{-1} and more than 300 µgL^{-1} cause toxicity in human [12, 13]. The penicillamine a chelating agent, is a trifunctional compound, containing of a thioalcohol, a carboxylic acid, and an amine that was used for the treatment of Wilson's disease, kidney stones , rheumatoid arthritis, and removal of heavy metal. Based on disorder of copper metabolism, copper accumulated in human body and the penicillamine extracted extra copper from body but, it can be removed the other essential metals from body [14, 15]. Many analytical methods such as electrothermal atomic absorption spectrometry (ET-AAS) [16], the flame atomic absorption spectrometry (F-AAS) [17] and the inductively coupled plasma optical emission/ mass spectrometry (ICP-OES, ICP-MS) [18] have previously used for the determination of cobalt in various water and food samples. Moreover, analytical techniques based on the above instruments cannot

enough to use for solving the difficulty matrices. For this purpose, the procedures must be developed for the separation and preconcentration of cobalt from samples. There are many methodologies for extraction cobalt from difficulty matrixes including, the magnetic solid phase extraction (MSPE) [19], dispersive micro-solid phase extraction (D-µ-SPE) [20], the liquid-liquid extraction (LLE), the dispersive liquid-liquid microextraction (DLLME) [21], the electrochemistry methods (ECM) [22], the cloud point extraction (CPE) [23] and the precipitation [24]. Recently, the ultra-assisted dispersive liquid-liquid microextraction (USA-DLLME) [25] has been used as one of the most practical methods for the separation of metal ions. The main advantages of USA-DLLME to other techniques are simple separation, high preconcentration, fast analysis, low time, high recovery and good enrichment factor (EF). The ionic liquid as green solvent plays critical role for collection of ligand and metals from samples into two phases; a IL/ligand phase and liquid phase of water samples. Metal ions can be extracted from aqueous solution into the small-volume IL/ligand phase with hydrophobicity, the more density than water samples and low solubility in water. In this study, the mixture of (2*S*)-2-amino-3-methyl-3-sulfanylbutanoic acid (penicillamine)/ (OMIM PF$_6$) /acetone have been used for extraction of cobalt from water samples by USA-DLLME at pH=6. The thiol and amine groups of penicillamine play an important role in the coordination of metals and have a strong complex with the cobalt ions [26]. In this study, this ligand was used as an ion carrier and as a chelating agent to cobalt ions accompanied with ionic liquid

2. Experimental
2.1. Instrumental Analysis
The cobalt (Co) value in water and digested food samples was determined by AT-FAAS (GBC, Aus). The air-acetylene was used for cobalt measurement by AT-FAAS. The atom trap accessory as SQT-AT devices is placed on the burner. In order to improve sensitivity, the upper end of a tubular flame was directed into a SQT which the source beam was passed. SQT-AT devices cause to increase the sensitivity of absorption

(ABS) per concentration before analysis. The limits of detection (LOD) were obtained at 0.05 and 0.13 mg L^{-1} for the AT-FAAS and FAAS, respectively. The HCL was adjusted by screws up to maximum energy. The AT-FAAS for cobalt determination was tuned by wavelength of 240.7 nm (7 mA). The aspiration of samples into FAAS was done by the auto-sampler (0.5-1 mL). The linear range for AT-FAAS was 0.15-6.0 mg L^{-1} for cobalt analysis. The working range for the AT-FAAS and F-AAS was obtained at 0.15-15 and 0.4-15 mg L^{-1} for cobalt, respectively. Graphite furnace accessory coupled to an atomic absorption spectrophotometer (GBC) was used for validation of cobalt in digested food and water samples. The pH of the samples was adjusted by favorite buffer solutions (Sigma, Germany) and determined by the Metrohm pH meter (Swiss). The phosphate buffers (Na$_2$HPO$_4$ and NaH$_2$PO$_4$) were used to adjust the pH from 6.0 to 8.0.

2.2. Reagents and Materials

The ultra-pure H$_2$SO$_4$, HCl, NaOH and HNO$_3$ solutions for cobalt analysis in food and water samples were prepared from Sigma Aldrich (Germany). The calibration solutions of Co(II) were made by dissolving 1.0 g of cobalt nitrate (Co(NO$_3$)$_2$) in 1 L of deionized water (DW) solution (2% HNO$_3$). The linear ranges of cobalt were daily prepared by standard solutions (1g L^{-1}, 1000 mg L^{-1}) and diluted by DW (Millipore, USA). All of the laboratory glassware was cleaned with nitric acid (5% v/v) and washed with DW for 10 times. ionic liquid of 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIM PF$_6$, CAS N: 304680-35-1), 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM] [PF$_6$], CAS N: 304680-36-2), 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM] [PF$_6$], [BMIM][PF6], CAS N: 304680-36-2), and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF$_6$], CAS N: 155371-19-0), acetone (CAS N: 67-64-1) and the penicillamine (CAS N: 52-66-4) were purchased from Sigma, Germany. The reagents of Na$_2$HPO$_4$ and NaH$_2$PO$_4$ (CAS N: 7558-79-4, 99.95%; CAS N: 7558-80-7, 99%) were prepared from the Sigma Aldrich, Germany.

2.3. Preparation of water and food samples

All food samples (Rice, Spinach, Broccoli, and Onion) were pulverized and then ground/ dried/ homogenized before analysis. Finally, the powder samples are converted to a uniform size and then place in the oven at 90 $^{\circ}$C for 3 h. After adding DW to food samples, the homogenization of sample was digested with microwave (Antom Paar, multi-wave) based on book catalog procedure. The food samples were digested at optimum conditions (200 $^{\circ}$C, 500 ps UV radiation). First, 1.0 g of food powder samples were placed in PTFE tube with surrounding ceramic tube of microwave and then, 5 mL of HNO$_3$ with 1 mL of H$_2$O$_2$ solution were added to samples. The powder samples were digested for 58 min and diluted with DW up to 50 mL before determination of cobalt by the USA-DLLME at pH=6. By microwave, the all cobalt forms in foods (organic foods) convert to Co(II) by induced oxygen combustion and total cobalt can be determined in food samples. All water samples prepared based on filtration (200 nm) and acidified with HNO$_3$ (2%) by the ASTM sampling method for water and storage in PE tube at -4^{0}C.

2.4. Procedure of cobalt extraction

The Co(II) ions were separated and preconcentrated based on the complexation of cobalt-penicillamine in water and food samples by the USA-DLLME procedure (Fig.1). Also, the total cobalt in food samples was determined based on penicillamine ligand by the AT-AAS. The penicillamine (0.12 g) dispersed into 180 mg of hydrophobic ionic liquid ([HMIM][PF$_6$] and 0.5 mL acetone and then, the mixture of ligand/([HMIM][PF$_6$] /acetone was injected into 50 mL of water or standard solution of cobalt (1.5-62 µg L^{-1}) by a syringe at pH=6. After sonication of samples for 5.0 min, the Co(II) ions were complexed by the thiol group of penicillamine ligand at pH of 6 [Co(II)←:SH─(2S)-2-amino-3-methyl-3-sulfanylbutanoic acid]. After the extraction process, the Co-ligand was trapped in the hydrophobic [HMIM][PF$_6$] at the bottom of a conical PE tube by centrifuging for 5 min (3500 rpm). The upper liquid phase was
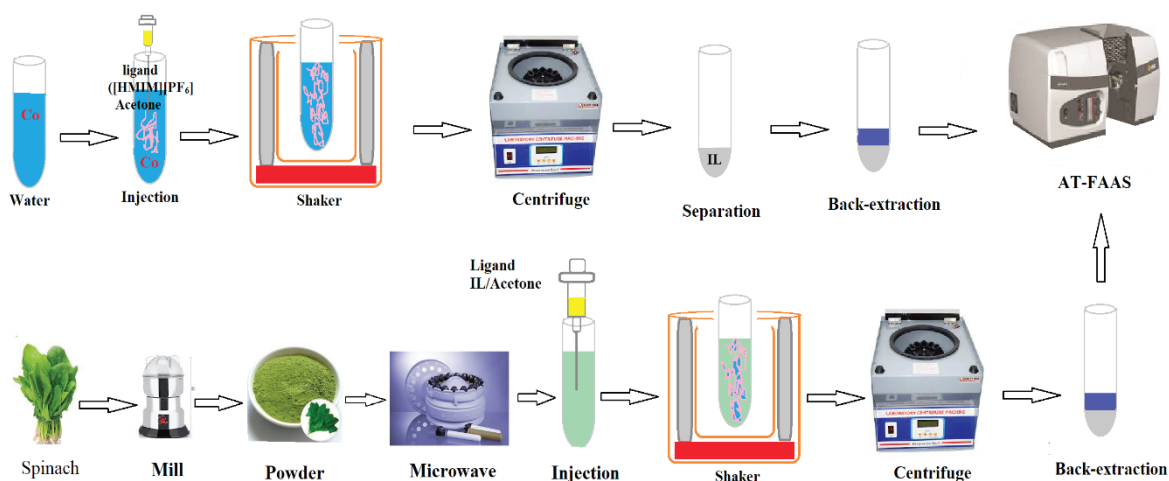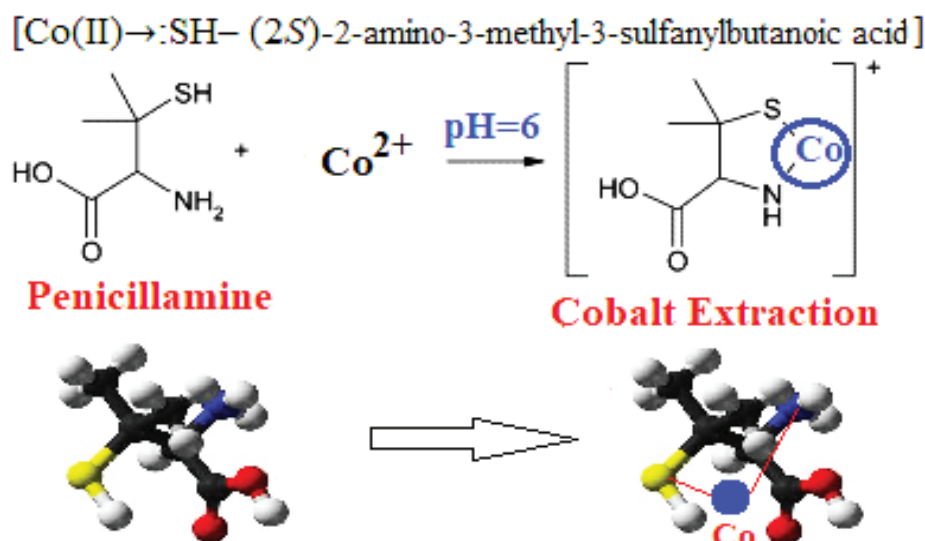
Fig.1. Cobalt extraction based on the complexation of penicillamine in water and food samples by the USA-DLLME procedure

evacuated and the Co ions were back-extracted from ligand/([HMIM][PF$_6$] into an aqueous phase by 0.25 mL of HNO$_3$ (0.5M) and diluted with DW up to 0.5 mL. Finally, the Co concentration in the remaining solution was determined by the AT-FAAS. In addition, 1.0 g of food powder was added to HNO$_3$/H$_2$O$_2$ solution (5:1) in the PTFE vials and samples were digested at 58 min based on the induced oxygen combustion/UV radiation. The digested food samples are diluted with DW up to 50 mL before cobalt analysis by the AT-F-AAS based on same procedure by ligand/([HMIM] [PF$_6$] /acetone at pH=6.

3. Results and Discussion

By the USA-DLLME procedure, the preconcentration/ separation of Co (II) ions in water samples was occurred for different cobalt concentrations as a lower range (1.5 μg L^{-1}) and upper range (62 μg L^{-1}) by the penicillamine ligand. Moreover, the total cobalt extracted from digested food samples such rice, spinach, broccoli and onion before determined by the AT-FAAS. The mechanism of extraction is based on the interaction of nitrogen(--NH) and thiol (--SH) groups of the penicillamine with cobalt ions using dative/covalent bonding (Schema 1). The results showed that efficient extraction of cobalt ion in water/food samples was performed by the

Schema 1. The mechanism of extraction between nitrogen and thiol of the penicillamine with cobalt ions

penicillamine ligand under optimized conditions such as the amount of the penicillamine ligand, pH, ionic liquids content, sample volume, and interfering ions

3.1. Amount of ligand

In the presented procedure, the amount of penicillamine as a ligand was optimized for separation/extraction of cobalt from the water and digested food samples. Thus, the amounts of penicillamine on cobalt extraction were studied in the range of 0.02-0.3 g in the presence of cobalt concentration (1.5-62 $\mu g\ L^{-1}$) for 50 mL of liquid samples. The results showed that the quantitative extraction was obtained at 0.10 g of penicillamine. So, 0.12 g of penicillamine was used as a final amount of ligand which was added to IL /acetone as an extraction phase for water and food samples. Also, the effects of ILs on the extraction of cobalt were examined without any ligand and the recovery of ILs for cobalt was achieved less than 5%. Due

to Figure 2, the cobalt was efficient extracted by complexation of penicillamine more than 95%.

3.2. Amount of ionic liquids/acetone

By the USA-DLLME procedure, the effects of different ionic liquids, [OMIM][PF$_6$], [BMIM][PF6] [HMIM][PF$_6$] and [EMIM][PF$_6$] were studied as trapping agents for cobalt extraction. So, the amounts of the hydrophobic ILs on the cobalt extraction were evaluated in the range of 20-250 mg of ILs containing 1.5-62 $\mu g\ L^{-1}$ of cobalt for 50 mL of water and digested food samples at pH=6. The quantitative recovery was achieved for cobalt with 160 mg [OMIM][PF$_6$]. So, 180 mg of [OMIM][PF$_6$] was used as an optimal IL for water and food samples. In addition, the effects of [OMIM][PF$_6$] for cobalt extraction were evaluated without any ligand and the maximum recovery was obtained less than 5%. Therefore, the [OMIM] [PF$_6$] as a trapper green solvent with highly efficient recovery can be collecting cobalt –ligand from the liquid phase (Fig. 3).
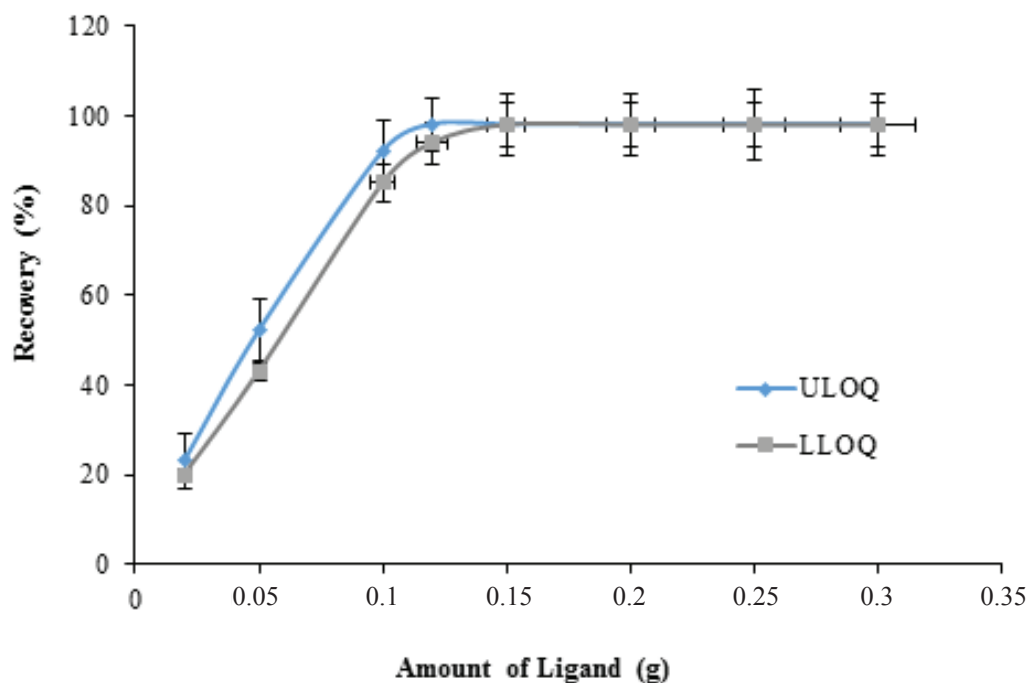

Fig.2. The effect of amount of penicillamine ligand on cobalt extraction by the USA-DLLME procedure (ULOQ: Upper Limit of Quantification, LLOQ: Lower Limit of Quantification)
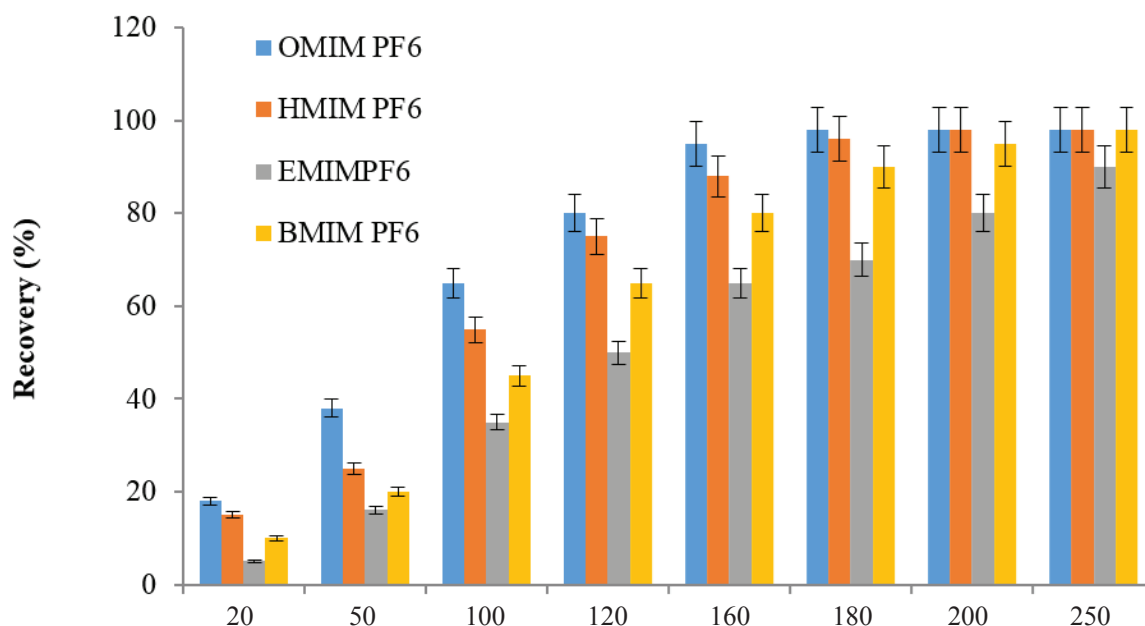
Fig.3. The effect of amount of IL on cobalt extraction by the USA-DLLME procedure

3.3. Sample volume

Sample volume is the main parameters for cobalt extraction in water and foods samples which must be optimized. Therefore, the different sample volumes for cobalt extraction/separation/preconcentration in water and foods samples between 5-100 mL based on penicillamine ligand were studied containing 1.5-62 μg L^{-1} of cobalt. According to Figure 4, the efficient extraction was obtained for 5-60 mL of water and food samples at pH=6. So, 50 mL of water or digested food samples were selected as an optimal volume by the USA-DLLME procedure (Fig. 4).
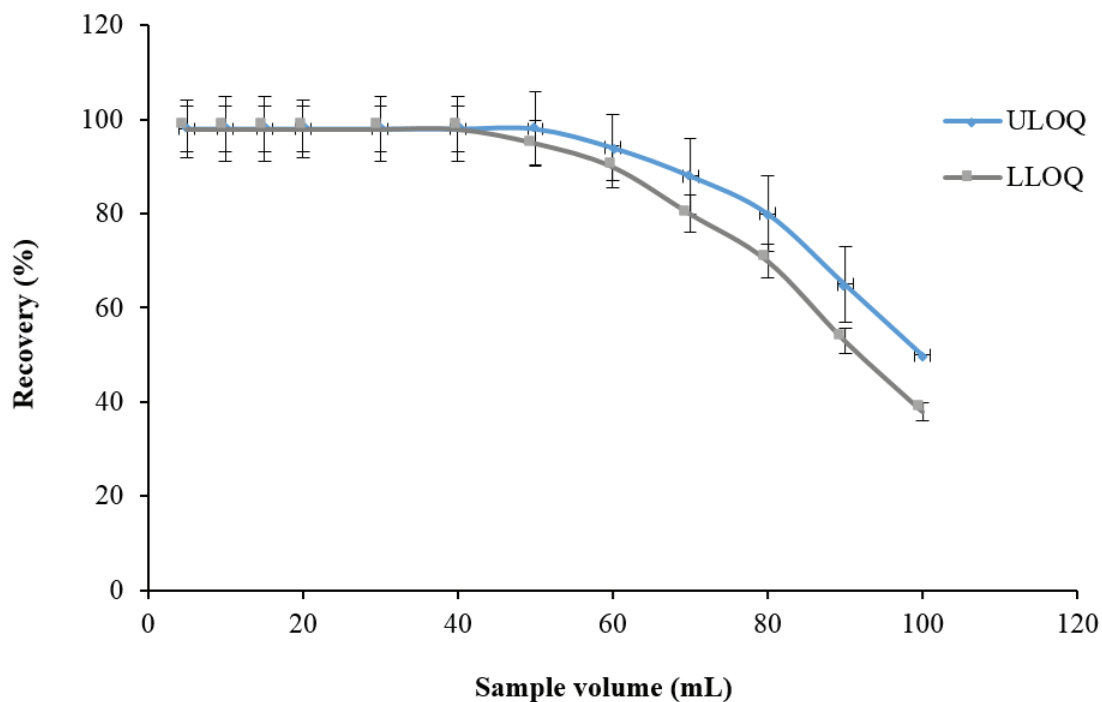

Fig.4. The effect of sample volume on cobalt extraction by the USA-DLLME procedure

3.4. pH Effect

pH is one of the most important parameters for cobalt extraction in water and digested food samples Therefore, the pH ranges from 2 to 10 was prepared and adjusted by buffer solution for cobalt extraction in aqueous samples. Efficient recovery based on penicillamine ligand /IL was observed for cobalt concentrations (1.5-62 μg L^{-1}) at pH of 5.5-6.5 in water samples. So, pH 6.0 was used for extraction of cobalt in water and digested food samples by the USA-DLLME procedure (Fig. 5). The proposed mechanism of cobalt extraction has been shown in the Schema 1 based on dative/covalent bond of thiol (HS) and amine (NH$_2$) functional groups of penicillamine with the positive charge of cobalt (Co^{2+}) at pH 6.0. Due to results, the isoelectric pH of penicillamine is 4.85, it can be concluded that above this pH, the amine and thiol groups of peniclamine are free and they have nucleophilic ability to attack to orbitals of cobalt ion, and they easily participate in the complex formation process to extract cobalt ion. So in acidic pH, the (NH$_2$) group of penicillamine ligand has positive charged (NH$_3^+$) and the complexation wasn't occurred due to electrostatic repulsion between Co^{2+} and NH$_3^+$, if some complexation is formed, it is due to the participation of the thiol group in this process. Also, the observed decline in the Figure 5 at pH above of 6.5 may be due to the competition of hydroxyl ions with the penicillamine ligand for complex formation resulting in the formation of stable cobalt hydroxide. So, the complexation of penicillamine ligand with Co^{2+} ions decreased at more than pH=6.5 as participated cobalt ions by hydroxide form (Co(OH)$_2$).

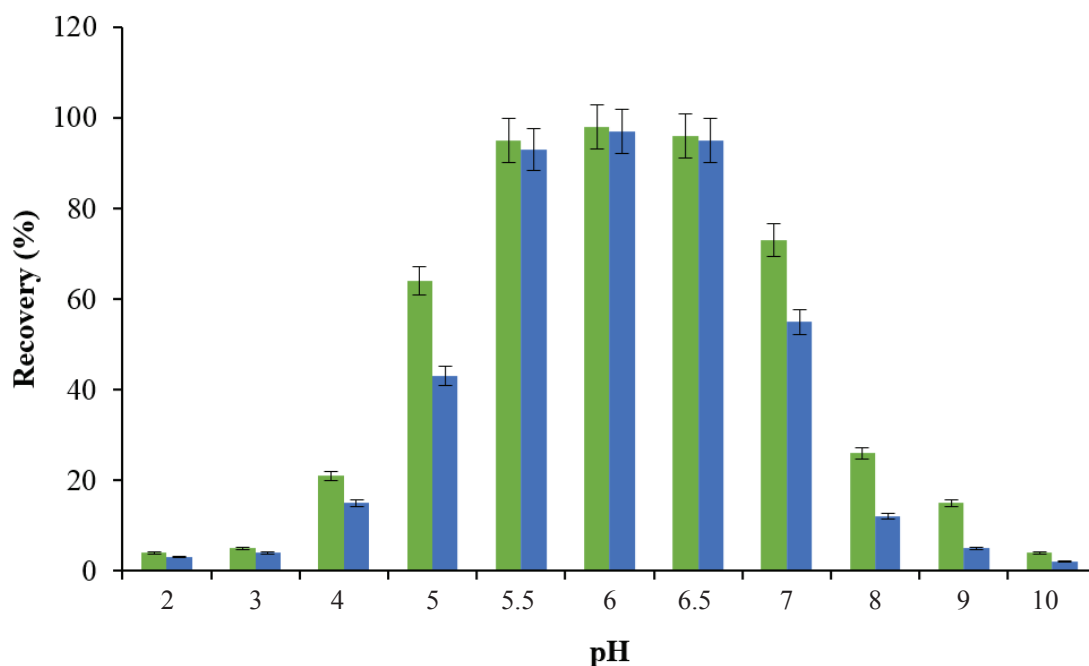**Fig.5.** The effect of pH on cobalt extraction at LLOQ (Blue) and ULOQ (green) by the USA-DLLME procedure

3.5. Effect of interference of ions

The effect of interference ions on cobalt extraction based on penicillamine ligand in water/food samples was evaluated by the USA-DLLME procedure. So, the main concomitant ions were studied in water and food samples with different concentrations between 0.5-3 mgL^{-1} for 50 mL of samples at pH=6. The results showed that the interfering ions had not affected for the cobalt extraction in water/food samples by the proposed procedure (Table 1). Also, the concentration ratio of interfering ions/cobalt ions (C_M/C_{Co}) for water ranged between 100-1800. The mean ratios for mercury, nickel and lead were seen at about 100-200, 700-850, 600-800 in water and digested food samples, respectively. So, the penicillamine ligand/ionic liquid phase can be extracted cobalt ions in the presence of the main interfering ions.

3.6. Eluent concentration and volume

The various eluents such as HNO_3, HCl and H_2SO_4 were used for back extraction of cobalt ions from the penicillamine ligand/IL/acetone. At acidic pH, the complexation of Co…SH-P was broken down and cobalt ions released into acid solution. Therefore, the various acid solutions based on different volumes and concentrations (0.2-1 mol L^{-1}, 0.1-1 mL were used for cobalt back extraction from IL phase. The Co(II) ions were quantitatively back-extracted from the penicillamine ligand/IL by HNO_3 with concentration more than 0.4 M. So, the 0.5 mol L^{-1} of HNO_3 solution was selected as an eluent. Moreover, the various volumes of eluents between 0.1-1 mL were used for back-extraction of cobalt ions in water/food samples. Due to Figure 6, the 0.25 mL of HNO_3 (0.5 M) had the efficient back-extraction of Co(II) ions from IL phase. Finally, the remained solution was diluted with DW up to 0.5 mL before determining by AT-FAAS.

Table 1. The effect of interfering ions on extraction of Co(II) in water and digested food samples by the USA-DLLME procedure

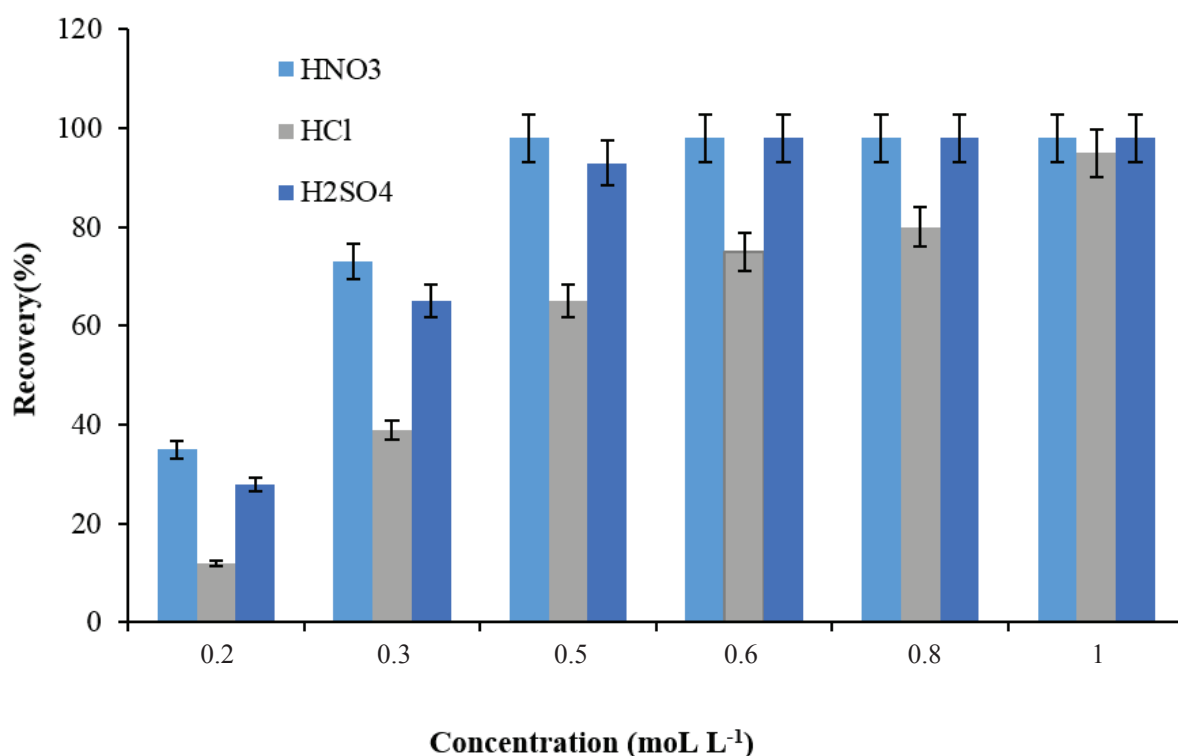| Interfering Ions in blood (M)	Mean ratio ($C_M/C_{Co(II)}$)	Recovery (%)
	Co(II)	Co(II)
Cr^{3+}, Al^{3+}, Fe^{3+}	750	97.0
Mn^{2+}, Cd^{2+}, Mo^{2+}	800	96.6
Pb^{2+}	700	99.4
Zn^{2+}, Cu^{2+}	600	97.8
I^-, Br^-, F^-, Cl^-	1200	97.4
Na^+, K^+, Ca^{2+}, Mg^{2+}	1400	98.1
CO_3^{2-}, PO_4^{3-}, $HCO3^-$, SO_4^{2-}	1000	99.2
Ni^{2+}	800	97.9
NH_4^+, SCN^-, NO_3^-	900	98.3
Hg^{2+}	150	97.2

Fig.6. The effect of eluents on cobalt extraction by the USA-DLLME procedure

3.7. Real sample analysis

The extraction of cobalt (II) ions with the penicillamine ligand in water/food samples were developed by the USA-DLLME procedure at pH 6. Also, the total Co(II) in rice, spinach, broccoli and onion was determined after the digestion process by proposed procedure. The total Co(II) determined in digested foods samples after extraction by the penicillamine ligand/[OMIM][PF$_6$] at pH 6.0. Moreover, the real water and food samples were validated by spiking of standard solutions of cobalt in optimized conditions (Table 2). Therefore, the various concentrations of Co(II) were spiked to real samples. The results showed us that the high recovery for Co(II) ions in water/food samples was created by 1.2 g of the penicillamine ligand and 150 mg of [OMIM][PF$_6$].

Based on Table 2, the efficiency extraction and the satisfactory results was demonstrated the penicillamine ligand/[OMIM][PF$_6$] can be obtained the accurate and precision results for cobalt in liquid samples. Also, the method

validation was achieved based on the ET-AAS and the ICP –MS analyzer by microwave digestion process (Table 3).

4. Conclusions

A simple and sensitive method based on the penicillamine ligand/[OMIM][PF$_6$] was obtained for the Co (II) ions determination in water and digested food samples at pH=6. The concentrations of cobalt ions were determined by the AT-FAAS detection method after sample preparation by the USA-DLLME procedure. Recovery was achieved between 95.2–103.6 and relative standard deviation (RSD%) between 1.9-4.5 under optimized conditions. In this procedure, the shaking and centrifuging time were 4.5 and 3.0 minutes, respectively. The working range of 1.5-153 µg L^{-1} were achieved by the presented method. Therefore, cobalt ions were extracted and determined effectively using penicillamine ligand/[OMIM][PF$_6$] in water/food samples with the USA-DLLME coupled to AT-FAAS.

Table 2. Validation of methodology for Co(II) determination with penicillamine ligand/[OMIM][PF$_6$] based on spiking standard samples by the USA-DLLME procedure coupled to AT-FAAS

Sample*	Added (µg L^{-1})	*Found W (µg L^{-1})/F(µg g^{-1})	Recovery (%)
Well water A	---	12.1 ± 0.4	---
	10	21.9 ± 0.9	98.0
Wastewater B	---	45.6 ± 2.3	---
	50	95.2 ± 4.5	99.2
Wastewater C	---	34.5 ± 1.7	---
	50	85.2 ± 3.9	101.4
Rice	---	21.2 ± 0.8	---
	20	40.9 ± 1.6	98.5
Spinach	---	24.6 ± 1.1	---
	25	49.2 ± 2.3	98.4
Broccoli	---	30.2 ± 1.2	---
	30	60.8 ± 2.4	102
Onion	---	27.8 ± 1.3	---
	30	57.3 ± 2.7	98.3

*Mean of three determinations of samples ± confidence interval (P = 0.95, n =10)
Food samples digested by Microwave and determined by proposed procedure
All food samples prepared from supermarket Tehran
Well water A: 25 mL of water prepared from Shahre Ray, Tehran
Wastewater B: 25 mL of water prepared from petrochemical industry, Tehran, Iran
Wastewater C: 25 mL of water prepared from paint factory, Arak, Iran
The linear range for 25 mL of water samples is 3-124 µg L^{-1}
Water: W (µg L^{-1}) and Food: F(µg g^{-1})

Table 3. The comparing of USA-DLLME /AT-FAAS method with ET-AAS and ICP –MS for cobalt determination in water and digested food samples (Mean, water (µg L^{-1})/ Food (µg g^{-1}), n=20)

Sample	Ψ ICP-MS	ET-AAS^Ψ	Ψ USA-DLLME	r*	r✾
Wastewater A	11.9 ± 0.1	12.6 ± 0.3	12.3 ± 0.4	0.77	0.70
Wastewater B	46.1 ± 0.9	44.9 ± 2.3	45.5 ± 2.4	0.81	0.73
Rice	21.6 ± 0.5	20.6 ± 1.0	21.3 ± 0.8	0.65	0.78
Spinach	24.1 ± 0.8	25.3 ± 1.3	24.6 ± 1.1	0.62	0.81
Onion	26.9 ± 0.7	29.1 ± 1.5	27.6 ± 1.3	0.59	0.74

*r: Correlation of ET-AAS with USA-DLLME /AT-FAAS method for cobalt determination (*n*=20)
✾r: Correlation of ICP-MS with USA-DLLME /AT-FAAS method for cobalt determination (*n*=20)
*Mean of three determinations of samples ± confidence interval (P= ۰/۹۵, *n*=20)

5. Acknowledgments

6. References

[1] D. J. Paustenbach, B. E. Tvermoes, K. M. Unice, B. L. Finley, B. D. Kerger, A review of the health hazards posed by cobalt, Crit. Rev. Toxicol., 43 (2013) 316–362.

[2] J. E. Gray, R. G. Eppinger, Distribution of Cu, Co, As, and Fe in mine waste, sediment, soil, and water in and around mineral deposits and mines of the Idaho Cobalt Belt, USA, Appl. Geochemistry, 27 (2012) 1053–1062.

[3] H. P. Hutter, P. Wallner, H. Moshammer, G. Marsh, Dust and cobalt levels in the austrian tungsten industry: workplace and human biomonitoring data, Int. J. Environ. Res. Public Health, 13 (2016) 931-938.

[4] M. Klasson, I. Bryngelsson, C. Pettersson, B. Husby, H. Arvidsson, H. Westberg, Occupational exposure to cobalt and tungsten in the swedish hard metal industry: air concentrations of particle mass, number, and surface area, Ann. Occup. Hyg., 60 (2016) 684–699.

[5] World Health Organization (WHO), Guidelines for drinking water quality, 3rd edn. World Health Organization, Geneva, 2011. https://www.who.int/publications-detail-redirect/9789241549950.

[6] S. Feng, X. Wang, G. Wei, P. Peng, Y. Yang, Z. Cao, Leachates of municipal solid waste incineration bottom ash from Macao: Heavy metal concentrations and genotoxicity, Chemosphere, 67 (2007) 1133–1137.

[7] S. R. Lim, J. Schoenung, Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays, J. Hazard. Mater., 177 (2010) 251–259.

[8] M. Moghadam, S. Jahromi, A. Darehkordi, Simultaneous spectrophotometric determination of copper, cobalt, nickel and iron in foodstuffs and vegetables with a new bis thiosemicarbazone ligand using chemometric approaches, Food Chem., 192 (2016) 424–431.

[9] Z. Tekin, S. Erarpat, A. Şahin, D. Selali Chormey, S. Bakırdere, Determination of vitamin B12 and cobalt in egg yolk using vortex assisted switchable solvent based liquid phase microextraction prior to slotted quartz tube flame atomic absorption spectrometry, Food Chem., 286 (2019) 500–505.

[10] K. A. Fox, T. M. Phillips, J. H. Yanta, M. G. Abesamis, Fatal cobalt toxicity after total hip arthroplasty revision for fractured ceramic components, Clin. Toxicol., 54 (2016) 874–877.

[11] A. Cheung, Systemic cobalt toxicity from total hip arthroplasties: review of a rare condition Part 1 - history, mechanism, measurements, and pathophysiology, Bone Joint J., 98 (2016) 6–13.

[12] B. Tvermoes, B. Finley, K. Unice, J. Otani, D. Paustenbach, D. Galbraith, Cobalt whole blood concentrations in healthy adult male volunteers following two-weeks of ingesting a cobalt supplement., Food Chem. Toxicol., 53 (2012) 432-439.

[13] A. Hart, P. Buddhdev, P. Winship, N. Faria, J. J. Powell, J. Skinner, Cup inclination angle of greater than 50 degrees increases whole blood concentrations of cobalt and chromium ions after metal-on-metal hip resurfacing, HIP Int., 18 (2008) 212–219.

[14] X. Zhang, D-penicillamine modified copper nanoparticles for fluorometric determination of histamine based on aggregation-induced emission, Microchim. Acta, 18 (2020) 7329.

[15] Y. Hong, S. Jo, J. Park, J. Park, J. Yang, High sensitive detection of copper II ions using D-penicillamine coated gold nanorods based on localized surface plasmon resonance, Nanotechnol., 29 (2018) 215501.

[16] Z. Tekin, T. Unutkan, F. Erulaş, E. G. Bakırdere, S. Bakırdere, A green, accurate and sensitive analytical method based on vortex assisted deep eutectic solvent-liquid phase microextraction for the determination of cobalt by slotted quartz tube flame atomic absorption spectrometry, Food Chem., 310 (2020) 125825.

[17] M. Shirani, F. Salari, S. Habibollahi, A. Akbari, Needle hub in-syringe solid phase extraction based a novel functionalized biopolyamide for simultaneous green separation/ preconcentration and determination of cobalt, nickel, and chromium (III) in food and environmental samples with micro sampling flame atomic absorption spectrometry, Microchem. J., 152 (2019) 104340.

[18] M. Asli, M. Azizzadeh, A. Moghaddamjafari, M. Mohsenzadeh, Copper, iron, manganese, zinc, cobalt, arsenic, cadmium, chrome, and lead concentrations in liver and muscle in Iranian Camel (Camelus dromedarius), Biol. Trace Elem. Res., 194 (2020) 390–400.

[19] S. G. Elci, Determination of cobalt in food by magnetic solid-phase extraction (MSPE) preconcentration by polyaniline (PANI) and polythiophene (PTH) coated magnetic nanoparticles (MNPs) and microsample injection system– flame atomic absorption spectrometry (MIS-FAAS), Instrum. Sci. Technol., 49 (2021) 258–275.

[20] F. Salimi, M. Shamsipur, E. Koosha, M. Ramezani, A new dispersive micro-solid phase extraction based on rejection property method combined with FAAS for the simultaneous determination of cobalt and copper after optimisation by Box-Behnken design, Int. J. Environ. Anal. Chem., (2020) 1–13.

[21] Q. Han, Y. Huo, X. Yang, Y. He, J. Wu, Dispersive liquid–liquid microextraction coupled with graphite furnace atomic absorption spectrometry for determination of trace cobalt in environmental water samples, Int. J. Environ. Anal. Chem., 100 (2020) 945–956.

[22] H. Kang, J. Li, C. Zhang, J. Lu, Q. Wang, Y. Wang, Study of the electrochemical recovery of cobalt from spent cemented carbide, RSC Adv., 10 (2020) 22036–22042.

[23] R. Kakitha, S. Pulipaka, D. Puranam, Simultaneous determination of iron and cobalt using spectrophotometry after catanionic mixed micellar cloud point extraction procedure, Orient. J. Chem., 36 (2020) 1168–1172.

[24] K. Kafumbila, Cobalt precipitation with MgO: material balance from kinetic samples cobalt precipitation with MgO: Material balance from kinetic samples. Independent Metallurgical Operations Pty Ltd (IMO), 2020.

[25] A. Ghasemi, M. R. Jamali, Z. Es'haghi, Ultrasound assisted ferrofluid dispersive liquid phase microextraction coupled with flame atomic absorption spectroscopy for the determination of cobalt in environmental samples, Anal. Lett., 54 (2021) 378–393.

[26] S. Keshipour, K. Adak, Magnetic d-penicillamine-functionalized cellulose as a new heterogeneous support for cobalt (II) in green oxidation of ethylbenzene to acetophenone. Appl. Org. Chem., 31(2017) e 3774. https://doi.org/10.1002/aoc.3774