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DETERMINATION OF COBALT AND NICKEL AFTER MODIFIED-COLD-INDUCED AGGREGATION MICROEXTRACTION BASED ON IONIC LIQUID IN HAIR AND WATER SAMPLES

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ABSTRACT. Modified-cold-induced aggregation microextraction(M-CIAME) as a separation and preconcentration method for Co^{+2} and Ni^{+2} ions determination based ionic liquid (IL) coupled to UV-Vis spectrophotometry is proposed. Cobalt and nickel were complexed with4-(2-pyridylazo)-resorcinol (PAR) as a chelating at pH 6. Then 60µL of 1-Hexyl-3-methylimidazoliumhexafluorophosphate [CMIM][PF_6] was injected to 10mL of sample solution. Afterward, the mixture was cooled in an ice bath and complex extracted in to ionic liquid phase. After centrifuging the extractant phase was analyzed using a spectrophotometric detection method.Several factors influencing the microextraction efficiency of Co^{+2} and Ni^{+2} ions such as: pH, concentration of chelating agent, extractant phase volume, extraction time and interfering effect, have been investigated. Under the optimum conditions, the detection limits (LODs) of the method were5.9 and 5.87 ngL^{-1} for Co^{+2} and Ni^{+2}, with the relative standard deviations (RSDs) for 59 ngL^{-1} (n=4) of Co^{+2} and Ni^{+2} were 1.85% and 1.24%. The developed method was applied to the determination of trace cobalt and nickel in water and hair samples with satisfactory results.

Keywords: *Cold-induced aggregation microextraction, Ionic Liquid, Cobalt, Nickel, UV-Vis spectrophotometry.*

1. INTRODUCTION

The determination of trace amounts of cobalt and nickel in biological and environmental samples are getting increasingly important in contamination monitoring studies. Nickel is the metal component of the enzymeurease [1] and a necessary partaker of metabolism of plants and some animals [2].

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Also, cobalt is an essential trace element in nature,having an important role in many body functions, as a component of vitamin B_{12}[3]. However, if both of metals ingest in high levels, these could be harmful to human health. UV-Vis spectrophotometry is relatively simple, cheap and available technique in many laboratories for heavy metal determinations. In the determination of traces of cobalt and nickel in biological and environmental samples, serious interferences often occur owing to matrix components. Therefore, several preconcentration methods have been reported for the separation and preconcentration of Co and Ni ions, such as: dispersive liquid–liquid microextraction (DLLME) [4-5], in situsolvent formation microextraction(ISFME) [6], classical liquid–liquid extraction(LLE) [7-8], Solidified floating organic drop microextraction (SFODME) [9], solid phase extraction(SPE) [10-12], cloud point extraction(CPE) [13-16] and liquid phase microextraction (LPME) [17]. Also preconcentration is a very important issue for obtaining of low limits of detection. Modified-cold-induced aggregation microextraction(M-CIAME) is a highly sensitive, efficient and rapid method for the preconcentration and determination of traces of organic and inorganic compounds in several samples. So it can easily settle a salt content of up to40% [18-19]. This procedure can effectively decrease the detection limit while eliminating matrix interferences [20-21].

Ionic liquids (ILs) are salts that are usually composed of organic or an inorganic anions and either large asymmetric organic cations. They as replacement solvents in the sample preparation, due to their unique chemical and physical properties, such as: negligible vapor-pressure, high stability, good extractability for metal ions [22-24]. ILs are regarded to have the potential to be alternative reaction media for" Green Chemistry"[25]. In this work, a green preconcentration and extraction of $Co^{+2}$and Ni^{+2}ions with complexation were carried out using 4-(2-pyridylazo)-resorcinol(PAR) as a chelating and an ion liquid(1-hexyl-3-methylimidazolium hexafluorophosphate [CMIM][PF_6]) as an extractant solvent based on modified-cold-induced aggregation microextraction (M-CIAME). This was followed by UV-Vis spectrophotometry.

2. RESULTS AND DISCUSSION

In this study, one variable at a time optimization was used to obtain the optimum conditions for the M-CIAME based IL. These conditions for preconcentration and determination of cobalt and nickel ions were: pH, volume of IL as an extractant, the concentration of the chelating agent, extraction time, centrifuge condition, salts concentration, which were investigated and optimized in order to achieve a high recovery and enrichment factor.

2.1. Effect of pH

pH plays an important and unique role on complex formation and subsequent extraction, as it defines the charge of the complex. The effect of pH on the formation of complex for cobalt and nickel was studied in the range of 2–9. Absorbance increased in the range 2-6 and then started to decrease, because PAR activity decreases in the acidic qualification due to protonation of oxygen and nitrogen. The results illustrated in Fig.1 showed that the absorbance at pH of 6was much stronger. Therefore, samples and standards were adjusted at pH6 before M-CIAME based IL procedure.

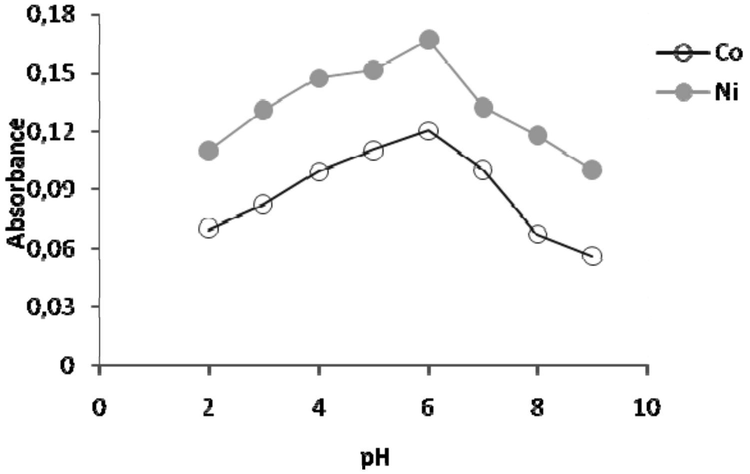

Figure 1. Effect of pH on cobalt and nickel extraction: sample volume, 10 mL; cobalt and nickel concentration, 59 ngL^{-1}.;PAR concentration,10^{-4} M; IL volume, 65µL;extraction time, 10min.

2.2. Effect of chelating agent concentration and IL volume

The influence of the amount of PAR on extraction efficiency of Co^{+2} and Ni^{+2} were studied and the experimental results are shown in Fig2. The absorbance Co^{+2} and Ni^{+2} incised by increasing the PAR concentration up to 4×10^{-4} $molL^{-1}$ of PAR and then decreased. So, a concentration of 4×10^{-4} $molL^{-1}$ was chosen as the optimum PAR concentration in order to achieve the highest possible extraction efficiency.

The volume of [CMIM][PF_6] that is used in this preconcentration procedure is a critical factor to obtain high extraction efficiency. Therefore, the effect of [CMIM][PF_6] volume on the performance of the microextraction procedure was studied within the range of 10-100 µL. By increasing the [CMIM][PF_6] volume, the absorbance of Co^{+2} and Ni^{+2} initially increased up to about 60-70µL of [CMIM][PF_6] and then started to decrease(Fig. 3). Thus, in order to achieve a good enrichment factor, low viscosity, 60 and70 µLof IL as optimum were chosen for Co^{+2} and Ni^{+2} respectively.

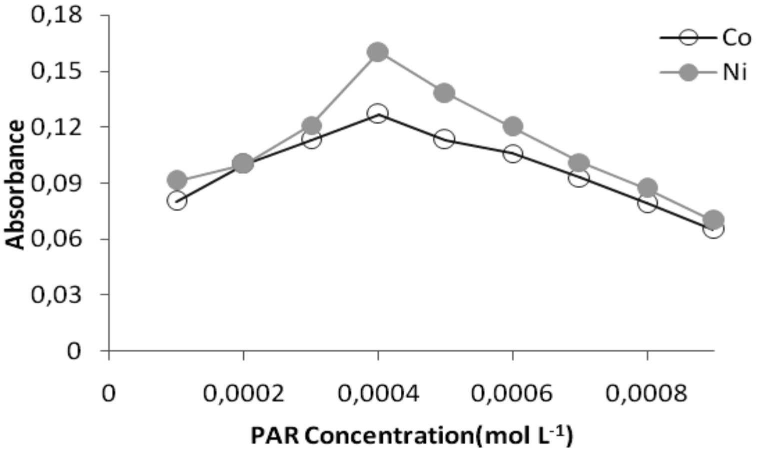

Figure 2. Effect of concentration PAR on cobalt and nickel extraction: sample volume, 10 mL;cobalt and nickel concentration, 59 ngL^{-1}; pH 6; IL volume, 65µL; extraction time, 10min**.**

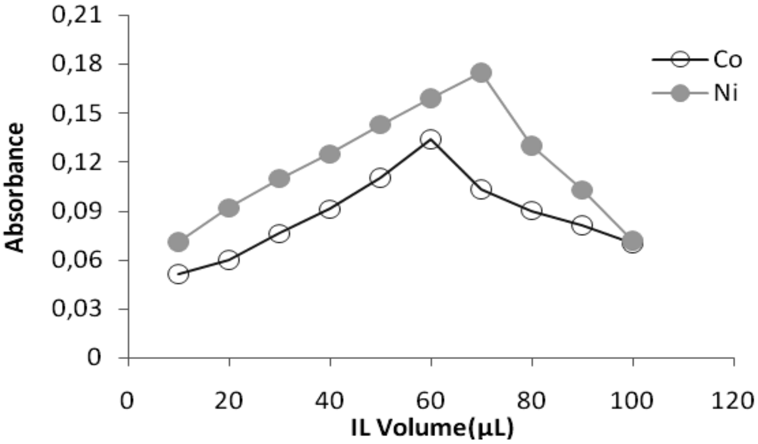

Figure 3. Effect of IL volume on cobalt and nickel extraction: sample volume, 10 mL; cobalt and nickel concentration, 59 ngL^{-1}.; pH6; PAR concentration, 4×10^{-4} M; extraction time, 10min.

2.3. Effect of temperature and extraction time

Optimal temperature is necessary to complete reactions, and to achieve easy and complete phase separation and preconcentration as efficient as possible [26]. Before shaking a solution containing IL, they were heated in the range of 20–60°C. So the temperature of 50°C for 4min was chosen. Because that the increase of temperature has no suitable effect up on the extraction efficiency.

In M-CIAME based IL, the extraction time is defined as the interval time between finishing the disruption of[CMIM][PF$_6$] and starting to centrifuge. Hence, extraction time plays an important role in this new procedure. In order to have excellent precision and high speed, it is essential; to select an extraction time that guarantees the attainment of equilibrium between aqueous and IL phase and maximize the extraction of analyte. The effect of extraction time was evaluated in the range of 5–25min. Fig.4 shows that the amount of complex extracted into IL phase increased with the increase of extraction time to15min. Therefore, a extraction time of 15min was selected in this work.

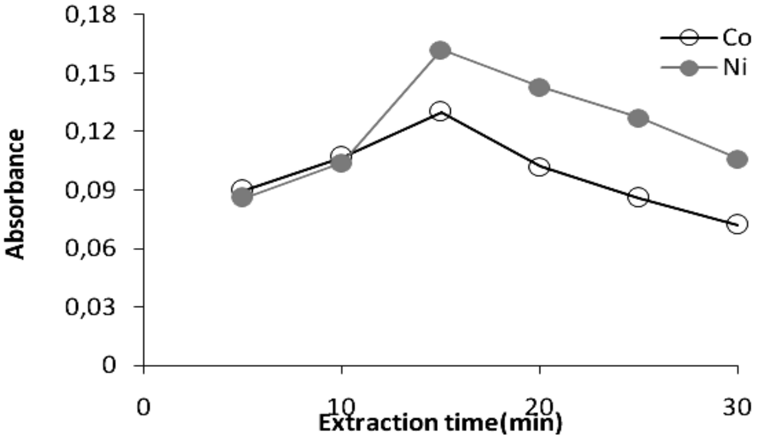

Figure 4. Effect of extraction time on cobalt and nickel extraction: sample volume,10 mL;cobalt and nickel concentration, 59 ngL^{-1}.; pH6; PAR concentration, 4×10^{-4} M; IL volume, 60μL.

2.4. Effect of centrifuge condition and salt content

The effect of centrifugation rate on the absorbance was studied in the range of 1000–6000rpm. It was found that over 4000rpm, IL-phase completely settled and a centrifugation time of 5 min at 5000rpm was selected for subsequent experiments, due to complete separation occurred at this time.

The effect of salt concentration on the extraction of Co^{+2} and Ni^{+2} was studied in the presence of $NaNO_3$ (10-60%W/V). Absorbance of Co^{+2} and Ni^{+2} decreased rapidly by increasing the salt concentration due to increase in solubility of [CMIM][PF_6]. Thus, concentration of 10% and 20% $NaNO_3$ (wv^{-1}) were selected for Co^{+2} and Ni^{+2}respectively in this work (Fig.5).

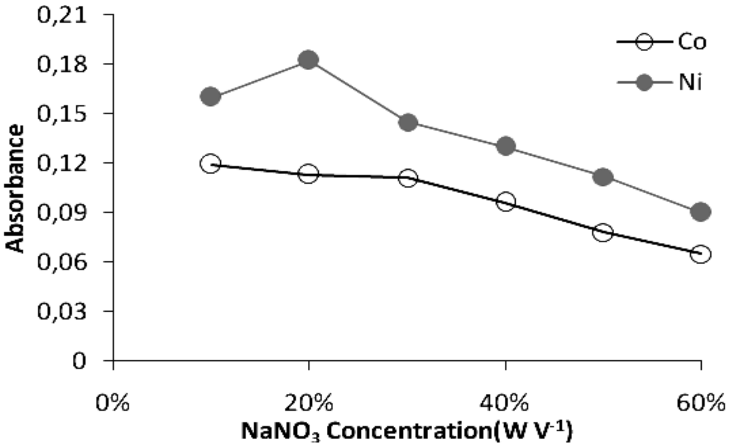

Figure 5. Effect of $NaNO_3$ on cobalt and nickel extraction:sample volume, 10 mL; cobalt and nickel concentration, 59 ngL^{-1}.; pH6; PAR concentration, 4×10^{-4} M;IL volume, 60µL; extraction time, 15min.

2.5. Interference study

The effect of diverse ions on the determination of Co^{+2} and Ni^{+} were studied according to the abovedescribed procedure. For this purpose, solution of 59 ngL^{-1} of studied analyte containing the corresponding interfering ions were prepared and operated according to the suggested procedure. The tolerable limit were defined the largest amount of foreign ions that produced an error not exceeding5% in the determination of Co^{+2} and Ni^{+2}. Most of cations and anions examined did not interference with the microextraction and determination of Co^{+2} and Ni^{+2}. The recoveries of Co^{+2} and Ni^{+2} were almost quantitative in the presence of all interfering ions in experiments, shown in Table1. All studied ions were found not interference from the coexisting ions for the determination of Co^{+2} and Ni^{+2}. Only Mn^{+2} interfered with the determination of Ni^{+2} in this experiment.

Table 1. Effect of foreign ions the recovery of cobalt and nickel(59 ngL^{-1})

Ni recovery(%)	Molar ratio(Ion/Ni^{+2})	Foreign ion	Co recovery(%)	Molar ratio(Ion/Co^{+2})	Foreign ion
92.3	1	**Cr^{3+}**	92.69	1	**Cr^{3+}**
88	1	**Mn^{2+}**	97.46	1	**Mn^{2+}**
91.42	100	**Mg^{2+}**	104	100	**Mg^{2+}**
98.81	1	**Co^{2+}**	98.41	1	**Ni^{2+}**
99.4	10	**Cu^{2+}**	96.82	10	**Cu^{2+}**
93.19	1000	**Na^{+}**	95.23	1000	**Na^{+}**
94.97	100	**K^{+}**	101	100	**K^{+}**
94.37	1	**Pb^{2+}**	95.87	1	**Pb^{2+}**
98.81	10	**Fe^{3+}**	102	10	**Fe^{3+}**
103	100	**Hg^{2+}**	101	100	**Hg^{2+}**
97.63	100	**Cl^{-}**	103	100	**Cl^{-}**
90	100	NO_3^-	104	100	NO_3^-
98.22	100	SO_4^{2-}	95.2	100	SO_4^{2-}

Table 2.1. Determination of Co^{+2} and Ni^{+2}inTap water

Metal	Added(ngL^{-1})	Found mean± SD[a] UV-Vis(ngL^{-1})	Recovery (%)	Found mean±SD (ET-AAS) (ngL^{-1})
Co	0	0. 59±0.017	-	-
	59	61.06±0.06	102.4	63.18
Ni	0	0.587±0.026	-	-
	58.7	60.5±0.064	102	59.11

[a] Standard deviation (n=4)

Table 2.2. Determination of Co^{+2} and Ni^{+2} in human and cow hairs(n=4)

Metal	Sample	Found mean± SD UV-Vis(μgg^{-1})	Found mean±SD (ET-AAS) (μgg^{-1})
Co	Human hair	1.65±0.07	1.70
	Cow hair	1.21±0.095	1.18
Ni	Human hair	1.83±0.054	1.82
	Cow hair	1.42±0.086	1.46

2.6. Figures of merit

Under the optimized experimental conditions,some parameters were investigated. The calibration curves were observed to be linear in the concentration range of(0.058-590µgL^{-1}) of Co^{+2} and Ni^{+2}. The correlation coefficient of the calibration curve equations was higher than0.990 for all elements. The detection limits calculated according to three times the standard deviation of the blank signals with the preconcentration step were 5.9 and 5.87 ngL^{-1}for Co^{+2} and Ni^{+2}respectively. Extraction recovery(ER) was calculatedaccording to the following given equation [29]:

Equation.1

$$\%ER = \frac{C_{ILPhase} \times V_{ILPhase}}{C_{aq} \times V_{aq}} \times 100$$

Enhancement of factors was obtained from the slope ratio of the calibration curve after and before preconcentration. The analytical characteristics of the methods are summarized in Table 3.

Table 3. Analytical characteristics of modified CLAME method

Parameter	Co^{+2} with preconcentration	Ni^{+2} with preconcentration
Correlation coefficient(R^2)	0.997	0.995
Limit of detection (ngL^{-1})	5.9	5.87
Enrichment factor(EF)	74	79.05
RSD % (n=4)	1.85	1.24
Extraction recovery (ER)	94	101

3. CONCLUSIONS

In this study, a new method of Modified-cold-induced aggregation microextraction(M-CIAME) based- ionic liquid solvent was successfully used for preconcentration and determination trace of cobalt and nickel by UV-Vis spectrophotometry in environmental and biological samples with good accuracy and reproducibility. This method is simple, environmentally friendly, selective, fast, safe and robust against very high content of salt (upto40%). Also our proposed method requires smallest volume of solvent while having good LOD and enhancement factor. This developed method was employed to determine cobalt and nickel ions in biological and environmental samples with satisfactory recovery.

4. EXPERIMENTAL SECTION

4.1. Apparatus

A lambda 25 UV-Vis spectrometer was purchased from Perkin-Elmer (USA). A100µL microsyringe(Hamilton) was employed to inject ionic liquid extracting phase to the sample solution. A (H-11 n) Kokusan Japan centrifuge was used to accelerate the phase separation process and aJeio Tech BW-05G water bath was used.

4.2. Reagents and materials

Standard stock solutions of Co^{+2} and Ni^{+2} at a concentration 1000 ppm were prepared by dissolving appropriate amounts of the pure nitrate salts in 100mL double distilled water. Solutions of lower concentrations were prepared daily by a suitable dilution of the stock solution with distilled water. Buffer solution with pH6 was prepared from 1.8 $molL^{-1}$sodium acetate solution and 0.1$molL^{-1}$ acetic acid solution by mixing the appropriate volumes of the two solutions and diluting to100mL. Acetic acid, sodium acetate and metal salts are all of analytical grade and purchased from Merck Chemical Company. A $4\times10^{-4}molL^{-1}$ PAR solution was prepared in deionized water and ethanol 50:50(v/v) (Aldrich Com) and also appropriate amounts of [CMIM][PF_6] was prepared in acetonitrile(Aldrich).

4.3. Modified CIAME procedure

For M-CIAME procedure 10mLof the sample solution containing Co^{+2} or Ni^{+2} and PAR (4×10^{-4} $molL^{-1}$) were adjusted to pH6 (acetate/acetic acid buffer) in a glass test tube with a conical bottom. Then, 60µL of [CMIM][PF_6] with a microsyringe was added to the solution. The tube was placed in a thermo stated bath at 50°C for 4min. The next step, the mixture was cooled in an ice bath for 10min, cloudy solution was immediately formed and metal ions was extracted in to the fine droplets of IL . Then separation of two phases was obtained by centrifugation for 5min at 5000rpm and IL-phase was diluted with 100µL ethanol and transferred to 350µL quartz cell for UV-Vis spectrophotometry determination.

4.4. Real samples preparation

The method was applied to tap water, human hair and cow hair sample from Tehran city. Standard hair samples were washed with 1% (w/v) (DDTC), 0.1M HCl and deionized water. The hair samples were firstly washed with HCL then one time with deionized water then with acetone and again one time with deionized water. Afterwards, the hair sample dried in oven at 70°C for 8 hours and then digested the next day [27]. Then 1g of washed hair samples were weighted and transferred to a teflon bombs and 10mL of concentrated HNO_3(65%) was added. The samples were heated on a plate about 100°C for 2h. After dissolution, the solution was allowed to cool and 5mL of H_2O_2 (30%) was added. The mixture was heated at(80°C for 2h). After digestion, the sample was diluted to final volume with deionized water and was treated according to the given procedure[28]. The results are show in Table2.

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