

Cloud Point Extraction, Pre Concentration and Spectrophotometric Determination of Nickel and Cadmium Ions

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Abstract

A simple, sensitive, rapid, and versatile cloud-point extraction (CPE) methodology has been improved for the preconcentration and determination of nickel and cadmium ions. The proposed method based on forming complexes with newly synthesized 6-(2-nitrophenylazo)-2-methyl-8-hydroxyquinoline [6-(2NPAM8HQ)] as a chelating agent to form hydrophobic complexes and Triton X-114 was selected as surfactant. The analyte was quantitatively extracted into the surfactant-rich phase and subsequently separated from the bulk aqueous phase by centrifugation and diluted with Ethanol and determined by UV/Visible spectrophotometry. The variables affecting the cloud point extraction such as pH, reagent concentration, surfactant concentration, equilibrium temperature, and time were optimized. The detection limit is 0.062 $\mu\text{g ml}^{-1}$ for nickel, and 0.047 $\mu\text{g ml}^{-1}$ for cadmium; the relative standard deviation for six replicate measurement is 0.84%, 1.04% for nickel and cadmium respectively. The proposed method was successfully applied to the determination of nickel and cadmium ions in rice samples available in the Iraqi market.

Keywords : 6-(2-nitrophenyl azo)-2-methyl-8-hydroxyquinoline, nickel, cadmium cloud point extraction, spectrophotometric determination,

Introduction

As the rapid development of industry, more and more wastewater containing hazardous heavy metal was discharged into river, which is harmful to living beings and the environment around [1]. Nickel is a moderately toxic element as compared with other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer [2]. Moreover, nickel can cause a skin disorder known as nickel eczema. The skin disorder can also appear in people who have great sensitivity to nickel, and can be caused by wearing jewels made of nickel alloys, like rings, chains, and bracelets [3]. Studies proved that women are more liable to this disease [4]. Medical diagnosis is currently established through nickel determination in blood and urine. Other studies show that disease incidence increased in patients who consume food rich in nickel. Cadmium is one of the most toxic elements and accumulates in humans mainly in the kidney, liver and lungs and is classified as a prevalent toxic element with biological half-life in the range of 10-30 years [5]. Daily intake of food and water is an important pathway through which cadmium enters the human body, thus there is increasing need to

monitor cadmium levels in food samples [6]. Moreover, such data can also provide us with information on the surrounding environment. However, direct determination of cadmium in food samples is often difficult, not only because of low concentration, but also because of matrix effects. To solve this problem, separation–preconcentration procedures are often involved prior to analysis [7]. Cloud point extraction is based on the property of most non-ionic surfactant in aqueous solutions to form micelles and become turbid when heated to a temperature known as cloud point temperature (T_c). When the temperature is higher than T_c , the micellar solution will be separated into a surfactant-rich phase of a small volume and a diluted aqueous phase [8]. CPE was applied to other determinations of diverse ions [9-12], different of nickel and cadmium, spectrophotometrically [13-29]. Table 1 shows some of these applications. This article presents the development of a procedure for the preconcentration of nickel and cadmium from different samples and its determination by UV/Vis spectrophotometry. This procedure is based on CPE of this metal into micellar media of octylphenoxypolyethoxyethanol surfactant (Triton X-114) after complexing this metal with 6-(2-nitrophenyl azo)-2-methyl-8-hydroxyquinoline.

Experimental

Instrumentation

UV Spectrophotometer Shimadzu UV – 1800. Japan, Thermosi water bath- England, pH meter WTW Terminal 740 – Germany, Triup International Corp 80-2 centrifuge, china.

Reagents and solutions

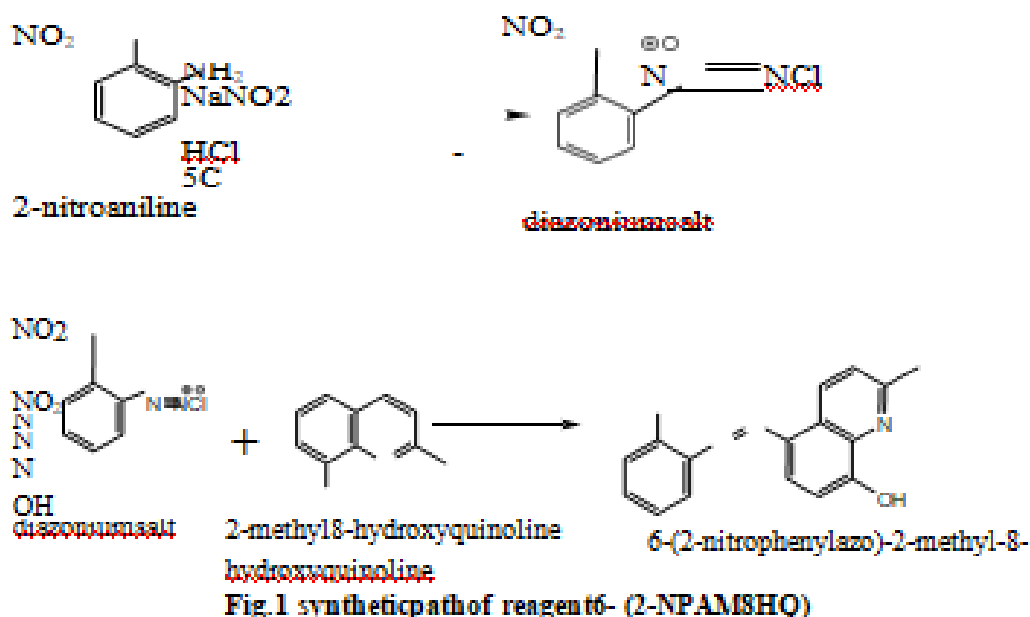
All chemicals and reagents used were analytical reagent grade, and were used without further purification. 1×10^{-3} M stock solution of 6-(2-nitrophenylazo)-2-methyl-

8-hydroxyquinoline was prepared by weighing (0.0154) g and dissolved in ethanol absolute in 50 ml volumetric flask. $1000 \mu\text{g ml}^{-1}$ stock standard solutions of Cadmium and nickel were prepared from cadmium nitrate $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ (0.6860 gm) in 250 ml of deionized water and nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (1.2388 gm) in 250 ml of deionized water. Triton x-114 solution concentration of (10% v/v) was used as stock solution.

Synthesis of 6-(2-nitrophenylazo)-2-methyl-8-hydroxyquinoline

[6-(2-NPAM8HQ)]

The synthesis of 6-(2-NPAM8HQ) was accomplished according to general procedure described elsewhere¹⁸ with some modifications of starting materials as shown in fig. 1



General procedure

5 ml analyte solution containing Nickel or Cadmium, for the nickel, 6-(2-NPAM8HQ) 10^{-4}M , 0.6 ml from 10% (v/v) triton x-114, pH adjusted to 6 and solution was placed in a water bath at 70°C for 25 min. phase separation was accelerated by centrifuging the resultant solution at 4000 rpm for 15 min. For cadmium 6-(2-NPAM8HQ) 10^{-4}M , 0.2 ml from 10% (v/v) triton x-114, pH adjusted to 5 and solution was placed in a water bath at 60°C for 20 min. phase separation was accelerated by centrifuging the resultant solution at 4000 rpm for 20 min, after cooling in an ice bath, a small volume of surfactant rich phase remained at the bottom of tube and diluted to certain volume of absolute ethanol. The nickel and cadmium contents were determined by UV/Vis spectrophotometry at 485 nm and 463 nm respectively against a blank solution.

Calibration was carried using different standard solutions of nickel and cadmium submitted to the same preconcentration and determination procedures. Blank solution was submitted to the same procedure and measured in parallel to the samples.

Samples preparation

Due to the biological and environmental significance of cadmium and nickel, four Rice samples were used to validate the accuracy of the proposed method. Rice samples were washed three times with deionized water and dried in oven at 100°C for 6 h. The dried samples were crushed, ground and then sieved and then digested with: 10 mL HNO_3 (2 M) and 10 mL HCl (2 M) into vessels, in which exactly 0.2 g of the Rice powder had been weighed and added. The pH was adjusted by addition NaOH solution (0.1 M). The mixture was heated and agitated on a rotary shaker (150 rpm, for 5 h); and applied the general procedure on the samples.

Results and discussion

Absorption spectra

The absorption spectra of Cd(II)- 6-(2NPAM8HQ) and Ni(II)- 6-(2NPAM8HQ) complexes were recorded in the presence of surfactants against a reagent blank prepared under the identical conditions. The spectra of Cd (II) and Ni (II) complexes show the absorption maxima of 463 and 485 nm obtained respectively while the ligand 6-(2NPAM8HQ) gave the absorption maxima of 395 nm as depicted in Fig.2.

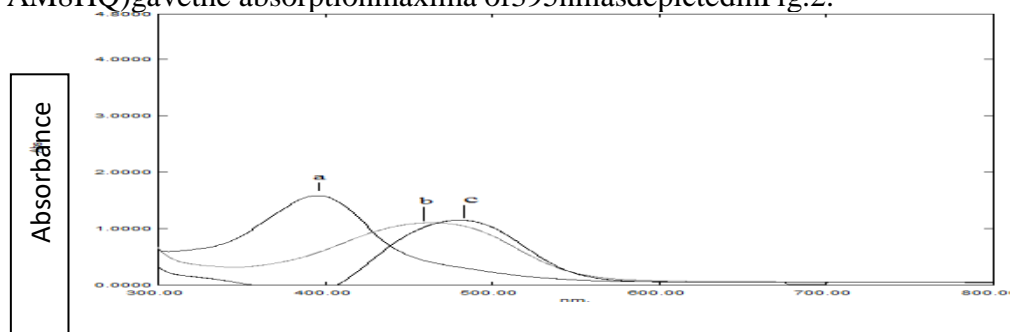


Fig.2. Absorption spectra (a) reagent 6-(2NPAM8HQ) = 10^{-4} M (b) Cd(II)-6-(2NPAM8HQ) complex (c) Ni(II)-6-(2NPAM8HQ) complex.

Effect of pH

The extraction of metal ion by CPE method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, in order to obtain the desired preconcentration. pH plays an important role in metal chelate formation. For this study, a pH range of 2-10 was used. Fig. (3 a, b) show the influence of pH on the absorbance of the [Cd(II)-6-(2NPAM8HQ)] complex and the [Ni(II)-6-(2NPAM8HQ)] complex. As can be seen, at pH 5 and pH 6 maximum extraction efficiency was obtained. Hence, pH 5, 6 was selected for cadmium and nickel respectively.

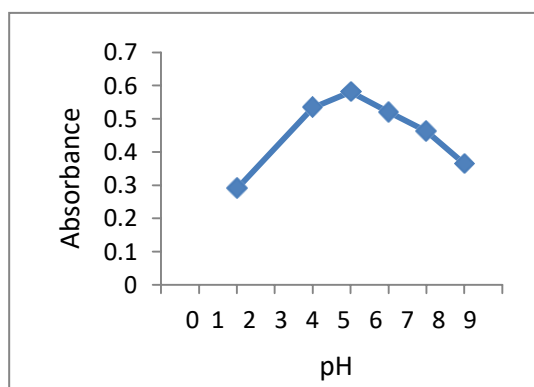


Fig.3(a) Effect of pH on formation of 2NPAM8HQ-Cd(II) complex at $\lambda = 463$ nm

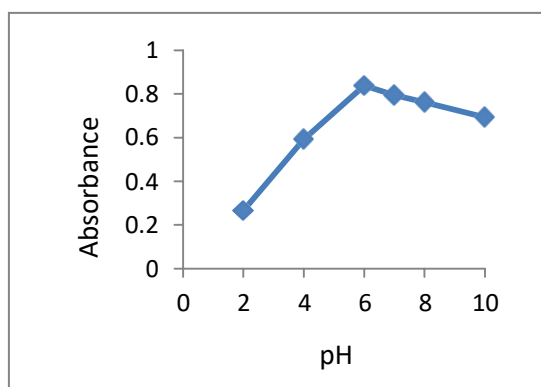
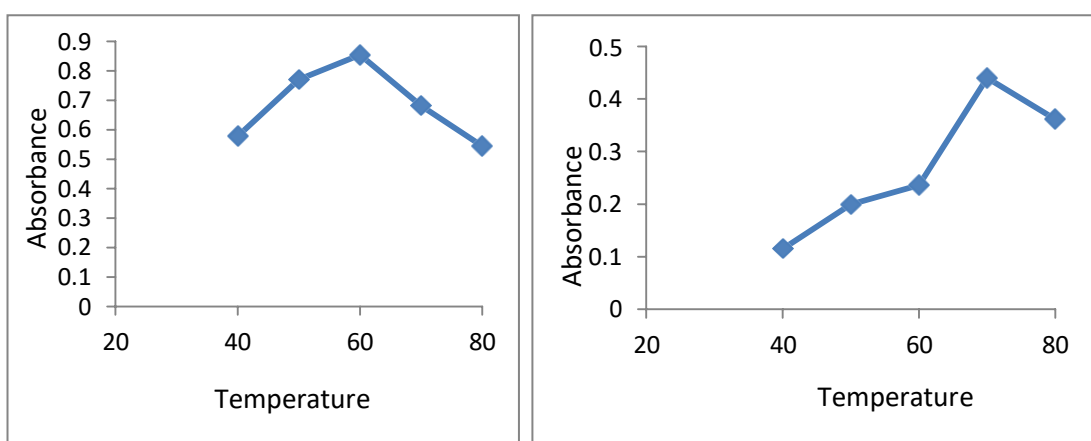


Fig.2 (b) effect of pH on formation of 6-(2NPAM8HQ)-Ni(II) complex. at $\lambda = 485$ nm

Effect of equilibration temperature and time

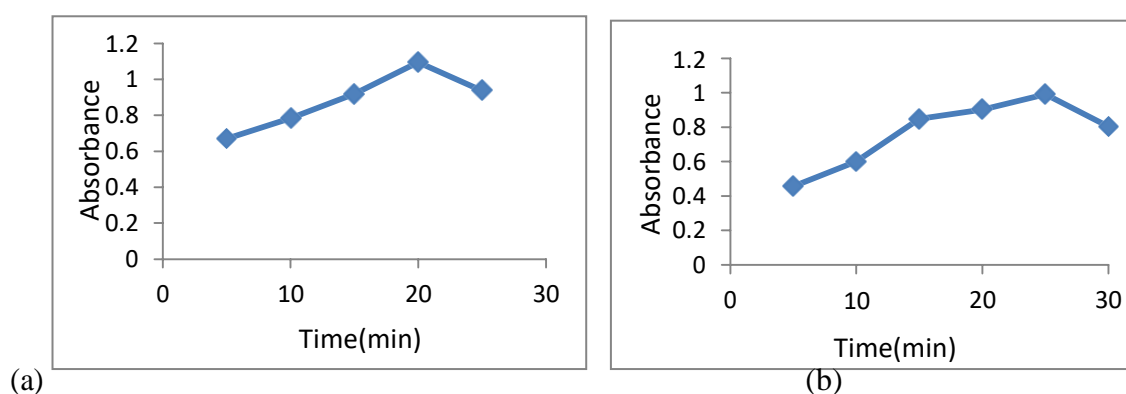
The greatest pre-concentration efficiency would achieve when the CPE process is carried out at the equilibration temperature above the cloud point temperature of the surfactant. In our work, the equilibration temperature of the thermostatic bath was investigated within the range of 40-80 °C (Fig. 4a, b). It is found that the temperature of 60 °C is adequate for cadmium and 70 °C for nickel. In addition, the effects of equilibration time on CPE were also researched. (Fig. 5 a, b) displays that the maximum absorbance for cadmium is obtained after 20 min and for nickel is obtained after 25 min. Therefore, the incubation time of 25 min and 20 min are chosen for the separation process of cadmium and nickel respectively.



(a)

(b)

Fig. 4 effect of equilibrium temperature (a) for cadmium(II), (b) for nickel(II).



(a)

(b)

Fig. 5 Effect of time of heating on formation of complexes with (a) cadmium(II),

(b) Nickel(II).

Effect of Triton X-114 amount

Compared with Triton X-100, Triton X-114 has lower cloud point temperature (18°C) and higher density of the surfactant-rich phase. It is more convenient for inducing the phase separation and collecting the surfactant-rich phase by centrifugation. Fig. 6 and Fig. 7 show the effect of variation of Triton X-114 amount on the absorbance signal for the determination of cadmium (II) and nickel (II). Different percentages 1% -20% and volumes of Triton X-114 (10% v/v) 0.1 – 1 ml were used in this study. As shown in Fig. 6 the maximum absorbance for Cd(II) and Ni(II) ions at (10% v/v) Triton X-114. In Fig. 7 0.2 ml (10% v/v) Triton X-114 for Cd(II) and 0.6 ml for Ni(II) selected as optimum concentration of Triton X-114.

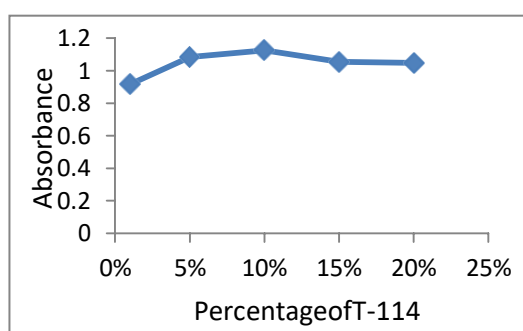


Fig.6(a) effect of Triton X-114 amount on Cd(II)

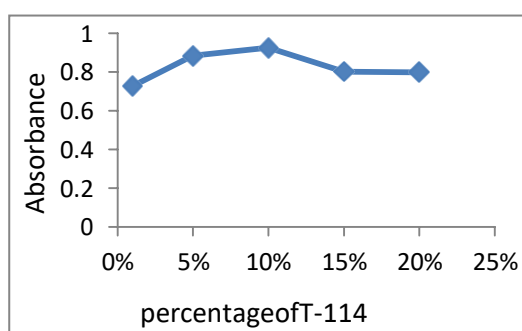
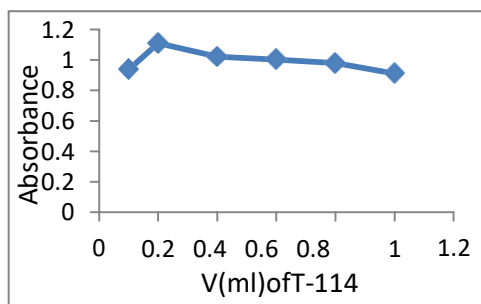
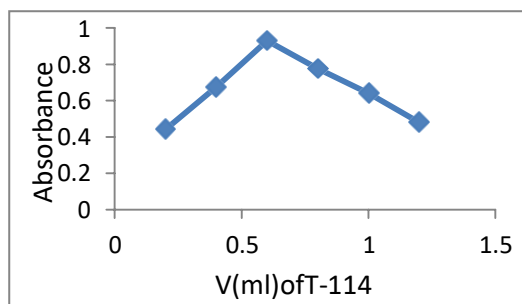


Fig.5 (b) effect of Triton X-114 on Ni(II).



(b)



(b)

Fig.7 Effect of Triton X-114 concentration (a) for cadmium (b) for nickel

Effect of 6-(2NPAM8HQ) concentration

The effect of 6-(2NPAM8HQ) on the CPE of Cd(II) and Ni(II) were investigated in the concentration range $0.01-0.1 \text{ mmol L}^{-1}$. The results were shown in Fig. 8. As it is seen for the Cd(II)-6-(2NPAM8HQ) and Ni(II)-6-(2NPAM8HQ) complexes, the signal increases up to a known concentration of 6-(2NPAM8HQ), which is considered as complete extraction. A concentration of 0.1 mmol L^{-1}

¹ was chosen as the optimum for both ions.

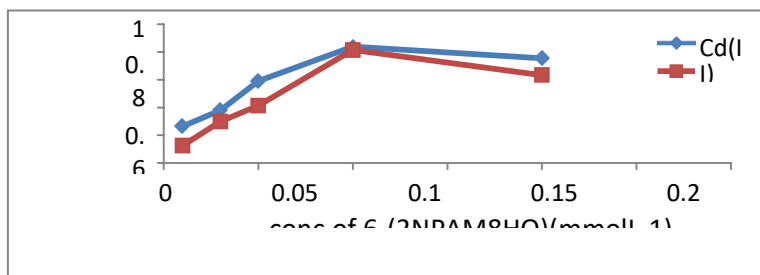


Fig.8 Effect of 6-(2NPAM8HQ) concentration on formation of complexes.

Calibration curves

Under the established optimum conditions a calibration curves was constructed by varying the concentration of the ions. The linear calibration curves shown in the Figs. 9 and 10 indicate that Beer's law is obeyed in the range of 0.5-30 µg/ml for Cd(II) and 1.0-30.0 µg/ml for Ni(II).

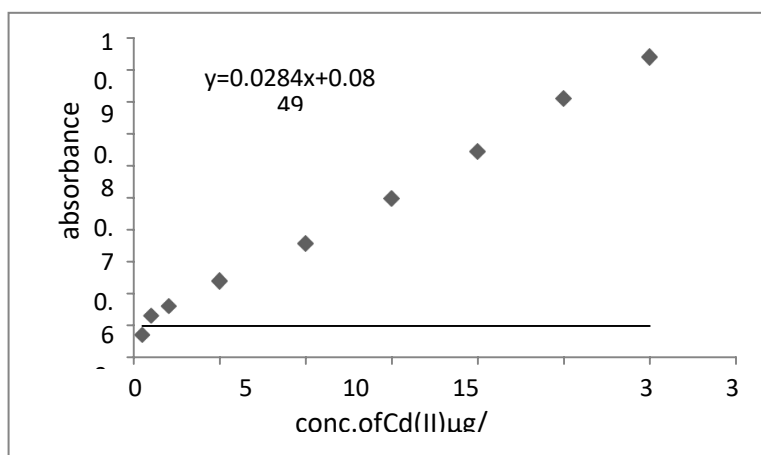


Fig.9 calibration curve of cadmium under the optimum conditions

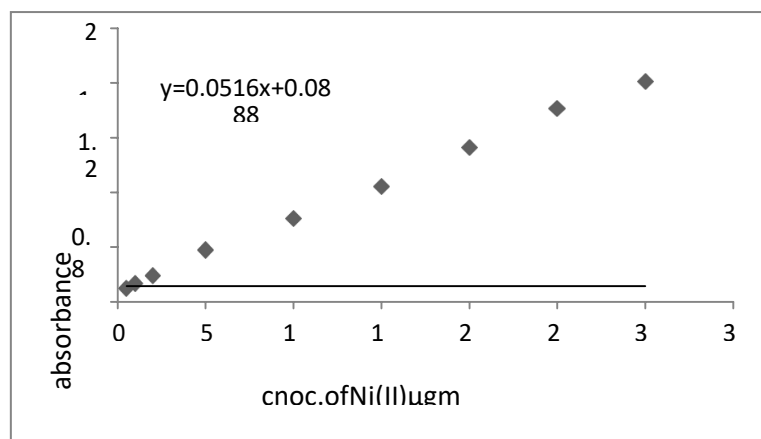


Fig.10 calibration curve of cadmium under the optimum conditions.

Interference studies

In order to study the selectivity of the proposed method, the effect of various cations and anions on the preconcentration and determination of $100 \mu\text{g mL}^{-1}$ Ni(II), Cd(II), were tested under the optimum conditions. The results are summarized in Table 2. Anion was considered as interferent, when it caused a variation in the absorbance of the sample greater than $\pm 5\%$. The results indicate that most of the cations and anions did not interfere even when present 1000-fold excess over analyte. Therefore, this cation would not interfere at higher concentrations. As can be seen in the table, a very good selectivity is achieved.

Table 1: some of the applications of CPE for determination of the different ions

Ions	Samples	Reagent	Surfactant	Technique	Ref.
$\text{Ni}^{2+}, \text{Zn}^{2+}$	Sea, river, mineral water	PAN	Triton X-114	FAAS	9
Co^{2+}	Pharmaceuticals	PAN and PAR	Triton X-114	FAAS	10
$\text{Fe}^{3+}, \text{Pb}^{2+}$	Vegetables	BPG	CTAB	UV-Vis	11
Hg^{2+}	Seafood	Methylgreen	Triton X-100	ICP-OES	12
Hg^{2+}	Fish	7-(6BrBTA8-HQ)	Triton X-114	UV-Vis	13
Cd^{2+}	Waters	DDTP	Triton X-114	ICP-MS	14
Cd^{2+}	Environmental	BIES	Triton X-114	FAAS	15
Cd^{2+}	Waters	TAN	Triton X-114	FAAS	16
$\text{Cd}^{2+}, \text{Pb}^{2+}$	Soils and food	BTABP, BPADPI	Triton X-100	UV-Vis	17
$\text{Cd}^{2+}, \text{Pb}^{2+}$	Honey	7-(6-MBT A8HQ)	Triton X-100	UV-Vis	18
Cd^{2+}	Drinking waters	TAC	Triton X-100	FAAS	19
Cd^{2+}	Urine	APDC	Triton X-100	WCAAS	20
Ni^{2+}	Waters	ACDA	Triton X-114	UV/Vis	21
Ni^{2+}	Saline oil-refinery effluents	Br-PADAP	Triton X-114	FAAS	22
Ni^{2+}	Foods	BDAP	Triton X-114	FAAS	23
Ni^{2+}	Environmental samples	IYPMI	Triton X-114	FAAS	24
Ni^{2+}	Water and food samples	Magneson	Triton X-114	FAAS	25

Table 2. Tolerance limit of foreign ions on the determination of $100 \mu\text{g mL}^{-1}$ of Ni(II) and $100 \mu\text{g mL}^{-1}$ of Cd(II).

Foreign ions	Tolerance ratio
Mg^{2+} , Ba^{2+} , Na^{+} , K^{+} , $\text{CH}_3\text{COO}^{-}$, Cl^{-} , SCN^{-} , NO_3^{-} , SO_4^{2-} , CO_3^{2-} , Br^{-} , Ca^{2+}	1000
3	
Cu^{2+} , Zn^{2+} , Co^{2+} , Fe^{3+}	100

Determination of cadmium and nickel in Rice samples

The proposed CPE–UV/Vis spectrophotometry methodology was applied to the determination of cadmium and nickel in four Rice samples purchased from local market. Table 3 shows the obtained results.

Table 3: Results obtained for the materials analysis

Samples	Nickel found by proposed method ($\mu\text{g/g}$)	Cadmium found by proposed method ($\mu\text{g/g}$)
American Rice	0.132	0.065
Iraqi Rice (A`anbar)	0.31	0.395
Thyland Rice	0.142	0.076
Indian Rice (Ahmed)	0.038	0.265

Conclusion

The determination of Cd(II) and Ni(II) in food samples was successfully performed by using cloud point extraction by applying 6-(2NPAM8HQ) as an extracting reagent. 6-(2NPAM8HQ) is a stable and selective complexing reagent. The proposed method is simple, rapid, safe, easy to use and inexpensive. In comparison with solvent extraction methods, this procedure employs only a small amount of surfactant which from the perspective of green chemistry is environmentally friendly materials. The method gives a very low limit of detection $0.062 \mu\text{g mL}^{-1}$ for nickel, and $0.047 \mu\text{g mL}^{-1}$ for cadmium; and good R.S.D values 0.84% , 1.04 % for nickel and cadmium respectively., and can be applied to the determination of Cd(II) and Ni(II) in various food samples.

2. References

- [1] Silva, E., Roldan, P., & Gine, M. (2009). J. Hazard. Mater. Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optical emission spectrometry, 171, 1133–

1138.

- [2] Nielsen,G.D.,Soderberg,U., Jorgensen, P.J., Templeton., DAI., Rasmussen, S.N.,Andersen, K.E.,Randjean, P.C. (1999). *Toxicol.Appl. Pharm.* 15467.
- [3] Kristiansen, J., Cristensen, J.M., Henriksen, T., Nielsen, NH., Menne, T. (2000). *Anal.Chim.Acta* 403, 265.
- [4] Ferreira, S., Santos, W.N., Lemos, V. A. (2001). *AnalyticChemicaActa, On-line preconcentration system forNickel determination in food samples by flame atomic absorption spectrometry*,445,145-151.
- [5] Davis,A.C., Wu,P., Zhang,X.F., Hou, X.D., & Jones,B.T. (2006)*DeterminationofCadmiuminBiologicalSamples, AppliedSpectroscopyReviews*,Vol.41,No.1, P. 35-75.
- [6] Davis,A.C., Zhang,W.P.,Hou,X.F.,&Jones,X.D. (2006).*Determinationofcadmium in biological samples. AppliedSpectroscopyReviews*, 41, 35–75.
- [7] Bosch Ojeda, C., Sánchez Rojas, F., Cano Pavón, J. M.(2010). *Preconcentration ofCadmium in Environmental Samples by Cloud Point Extraction and DeterminationByFAAS*, American Journal ofAnalyticalChemistry, 1,127-134.
- [8] Stalikas, C.D. (2002). *Micelle-mediated extraction as a tool for separation andpreconcentrationinmetal analysis. TRAC*, 21, 343-355.
- [9] Mssa, O. Yussra, GhaliAzhar, A., Hussein Ashwaq, S. (2020). *Cloud pointextraction,preconcentration And spectrophotometric determination of Co(II) and Cu(II) using 15-crown-5*, Indian journal of forensic Medicine and Toxicology., vol.14.No.1
- [10] ShathaTareh, S., Sarah Ali, M., SaifRadhi, S., &Hyfaa Mubarak, A. (2021). *Cloud point extraction Method for determination nickel in different water sample using An imidazole Derivative*, Nat.volatiles and Essent.Oils , 8(4) 1936-1952
- [11] Dalal Al-yousefi, A., &Ibtehaj Ali, R. (2022). *Spectrophotometric determination of Transition Elements by cloud point extraction with use laboratory by thiazolazoReagent and applied In environmental sample*, AIP conference proceedings 2386 , 03007
- [12] .Ali, S., Ali, I.. (2020). *Cloud point extraction and determination of Nickel(II)ions Complex in real Samles using new azo reagent*. Ressearch J. in advanced science, 1, 2,7-18
- [13] Oliveros, M ., Pavon, O., Codero,J.L. (1998). *Cloud point preconcentration and FlameatomicabsorptionSpectrometryapplicationtothedeterminationnickelAndzinc*,J.Anal. At. Spectrom, 13, 547-550
- [14] Manzoori, J., Zadeh, A. (2007). *Extraction and preconcentration of Lead using Cloudpoint technology, application to its determination in real samples by flame Atomicabsorptionspectrometry"*, ActaChim. Slov, 54, 378-384
- [15] Madrakian, T., &siri,R.(2011). *Spectrophotometricdeterminationof Fe³⁺ andPb²⁺ inreal samples after Micelle-Mediated Extraction*, ActaChim. Slov, 58, 288-294.
- [16] Li,Y.,& Hu,B. (2007).*Sequential cloud point extraction for the speciation of Mercury In seafood by Inductively Coupled Plasma Optical Emission Spectrometry*, Acta, B,62, 1153-1160.
- [17] Khammas,Z.,Ghali,A.(2013). *CloudPointExtractionProcedurefortheDeterminationof*

- Mercury by Spectrophotometry Using a New Synthesized Ligand*, Iraqi National Journal of Chemistry, volume 49, 25-37.
- [18] Da Silva, M., Frescura, V., & Curtius, A.J. (2000). *Determination of Trace Elements in Water Samples by Ultrasonic Nebulization Inductively Coupled Plasma Mass Spectrometry after Cloud Point Extraction*, *Spec-trochimica Acta B*, Vol. 55, No. 7, P. 803-813.
- [19] Ghaedi, M., Shokrollahi, A., Niknam, K., Niknam, E., Najibi, A., & Soylak, M. (2009). *Cloud Point Extraction and Flame Atomic Absorption Spectrometric Determination of Cadmium(II), Lead(II), Palladium(II) and Silver(I) in Environmental Samples*, *Journal of Hazardous Materials*, Vol. 168, No. 2-3, P. 1022-1027.
- [20] Silva, E. L. & Dos, P., Roldán, S. (2009). *Simultaneous Flow Injection Preconcentration of Lead and Cadmium Using Cloud Point Extraction and Determination by Atomic Absorption Spectrometry*, *Journal of Hazardous Materials*, Vol. 161, No. 1, P. 142-147.
- [21] Jawad, Sh., & Muslim, J. (2012). *Cloud Point Extraction Methodology for Separation and Microamounts Determination of Lead(II) and Cadmium(II) ions*, Iraqi National Journal of Chemistry, vol. 47, 401-412.
- [22] Khammas, Z., Ghali, A., & Kadhim, K. (2012). *Combined cloud-point extraction And spectrophotometric detection of lead and cadmium in honey samples using a New ligand*, *Int. J. Chem. Sci.*: 10(3), 1185-1204.
- [23] Portugal, L.A., Ferreira, H. S., Santos, W.N. L., Ferreira, & S. L.C. (2007). *Simultaneous Pre-Concentration Procedure for the Determination of Cadmium and Lead in Drinking Water Employing Sequential Multi-Element Flame Atomic Absorption Spectrometry*, *Microchemical Journal*, Vol. 87, No. 1, P. 77-80.
- [24] Donati, G.L., Pharr, K.E., Calloway, C.P. Jr., Nóbrega, J.A., & Jones, B.T. (2008). *Determination of Cd in Urine by Cloud Point Extraction—Tungsten Coil Atomic Absorption Spectrometry*, *Talanta*, Vol. 76, No. 5, P. 1252-1255.
- [25] Safavi, A., Abdollahi, A., Nezhad, M., Kamali, R. (2004). *Cloud point Extraction preconcentration and simultaneous spectrophotometric Determination of nickel and cobalt in water samples*, *Spectrochim Acta A*; 60:2897-2901.
- [26] Bezerra, A., Conceicao, M., Ferreira, A., Sérgio, L. (2004). *Doehlert matrix for optimisation of procedure for determination of nickel in saline oil-refinery effluents by use of flame atomic absorption spectrometry after preconcentration by cloud-point extraction*, *Anal Bioanal Chem*; 378, 798-803.
- [27] Azevedo Lemos, V., Selis Santos, M., Teixeira David, G., Vasconcelos Maciel, M., Bezerra, M. (2008). *Development of a cloud-point extraction method for Copper and nickel determination in food samples*, *J. of Hazard Mater*, 159, 1, 245-251.
- [28] Ghaedi, M., Shokrollahi, A., Niknam, K., Niknam, E., Soylak, M. (2009). *Development of efficient method for preconcentration and determination of copper, nickel, zinc and iron ions in environmental samples by combination of cloud point extraction and flame atomic absorptions spectrometry*, *Cent. Eur. J. Chem*, 7, 148-154.
- [29] Sahin, C., Efecinar, M., Satiroglu, N. (2009). *Combination of cloud point Extraction and flame atomic absorption spectrometry for preconcentration and Determination of nickel and manganese ions in water and food samples*, *J. Hazard Mater*, 176, 672-677.