

SIMULTANEOUS PRECONCENTRATION AND DETERMINATION OF Cu²⁺, Ni²⁺ AND Cd²⁺ BY MICELLE MEDIATED EXTRACTION IN FOOD AND WATER SAMPLES

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ABSTRACT

An effective extraction procedure based on the complexation of Cu²⁺, Cd²⁺, and Ni²⁺ with dithizone and extraction of these complexes by Tergitol NP-7 surfactant was developed. Micelle mediated extraction parameters such as pH, ligand and surfactant concentration, incubation time and temperature were investigated and optimized. Effects of external and internal interfering ions, linear dynamic range, detection and quantitation limits were examined and determined under optimal conditions. Detection limits were found as 0.5, 1.8 and 2.0 mg L⁻¹ for Cu²⁺, Ni²⁺ and Cd²⁺, respectively. Linear dynamic range values were between 0.125-2, 0.125-2.5 and 0.05-1.4 µg mL⁻¹ for Cu²⁺, Ni²⁺ and Cd²⁺ ions, respectively. Applicability, accuracy and precision of the method were checked with standard reference materials and real sample analyses by analyte addition technique. Finally, optimized method was applied to determine Cu²⁺, Ni²⁺ and Cd²⁺ contents of standard reference materials, mushrooms and water samples. Quantitative and accurate results were obtained from the analysis of standard reference materials and real samples.

Keywords: Micelle mediated extraction, Dithizone, FAAS, Heavy metals, Tergitol NP-7.

1. INTRODUCTION

Existence of metal ions in aquatic media can cause many environmental problems and in some cases deterioration of ecosystems. The increasing industrial activities and improper management of some sources may cause the accumulation of these pollutants [1].

The toxicity, persistence and non-biodegradable characteristics of trace metals such as cadmium (Cd²⁺), copper (Cu²⁺), nickel (Ni²⁺), etc., have attracted a great deal of worldwide attention². Their persistence and accumulation in environment tend to concentrate in the food chain which is a definite hazard for human and nature³.

For example the Cd²⁺, involves nausea, vomiting, diarrhoea and causes cramps in short terms, while it may damage kidneys, livers and blood in long-term exposures⁴. Although nickel and copper are considered as essential trace elements, their toxic effects are well known. Ni can be considered as one of the most common materials causes of allergic contact dermatitis and respiratory system diseases⁵, on the other hand the copper containing compounds may potentially affect the damages in cellular lipids, nucleic acids, proteins and carbohydrates in the long term exposures⁶. Because of the adverse effects of these heavy metals, they should be determined and removed from natural samples.

1,5-diphenylthiocarbazon (dithizone) is known as a strong chelating agent and forms complexes with soft metals such as Cu²⁺, Cd²⁺⁷ and also forms stable complex with Ni²⁺⁸. Therefore, dithizone is a potentially useful chemical for preconcentration and determination of trace metal ions in analytical chemistry⁹⁻¹⁰.

There are several techniques in literature for preconcentration and determination of metal ions from aquatic media. Some of the most investigated ones are solid phase extraction¹¹, liquid-liquid extraction¹² and micelle mediated cloud point extraction¹³.

Micelle mediated extraction (MME) is a unique technique which is based to form separable micelle surrounded metal and/or metal complexes above a certain temperature by using surfactants. When the temperature of the solution rises above the cloud point (at which the solution becomes cloudy), it is possible to separate into two phases: a surfactant rich phase including the target analytes and an aqueous phase. Two important properties for MME are the critical micellar concentration where the surfactant molecules become associated to form micelles¹⁴ and the cloud point temperature above which the solution becomes turbid¹⁵.

The aims of the study were to investigate the optimal parameters for simultaneous MME (by using the Tergitol® type NP-7 (TNP-7) non-ionic surfactant which has a low cloud point temperature of 20 °C at 1 w/w %) of Cu²⁺, Ni²⁺ and Cd²⁺ after their complexation with dithizone (C₁₃H₁₂N₄S) and their determination by flame atomic absorption spectrometry (FAAS). To the best of our literature survey this is the first attempt of the simultaneous preconcentration and determination of Cu²⁺, Cd²⁺ and Ni²⁺ by using TNP-7 in CPE.

2. Reagents and solutions

Doubly distilled water was used in all experiments. Metal ions containing stock solutions were prepared from high purities of nitrate and chloride salts of corresponding elements. Methanol, hydrogen peroxide, hydrochloric acid and nitric acid (Merck, Darmstadt, Germany) were used for dilution of surfactant bulk phase and digestion of solid samples. All buffer chemicals were purchased from Sigma-Aldrich (USA). Phosphoric acid and mono hydrogen phosphate for pH 2-3, acetic acid and sodium acetate for pH 4-5, mono hydrogen phosphate and di hydrogen phosphate for pH 6-8 were used for preparation of buffer solutions which have 0.2 mol L⁻¹ of ionic strength. TNP-7 which is commonly described as an alkylaryl polyether alcohol was used as source of micelles and purchased from Sigma-Aldrich (USA). Stock 1x10⁻³ mol L⁻¹ of complexing agent dithizone (Merck, Darmstadt, Germany) solution was prepared in 0.05 mol L⁻¹ NaOH.

2.1. Instruments

A Shimadzu AA 7000 flame atomic absorption spectrometer (Shimadzu, Japan) was used to measure the concentrations of metal ions. The pH adjustments were performed by using Hanna HI 2211 model pH-meter (Hanna, USA). Digital controlled thermostatic water bath (Nuve, Ankara, Turkey) was used to achieve the desired temperature of solutions. The centrifugation and separation of surfactant rich phase were achieved by Nuve FN 400 model centrifuge (Nuve, Ankara, Turkey). 1 and 5 mL of cleavable automatic transfer pipettes (Brand, Germany) were used to transfer precision amount of metal, ligand and surfactant solutions.

2.2. Micelle mediated extraction procedure

An aliquot of 10 mL of phosphate buffer solution was added to the analytical solution containing the analytes 1 µg of Cu²⁺, 2 µg of Ni²⁺ and 0.8 µg of Cd²⁺ and 1.0 ml dithizone was added to this solution from 3.0x10⁻³ mol L⁻¹ stock. After complexation, TNP-7 surfactant was added to a final concentration of 0.14% (w/v). The final volume of the solution was completed to 50 mL with distilled water. The model solutions were transferred to centrifuge tubes and kept for 10 min in thermostatic bath at 25 °C to achieve the process of extraction and preconcentration of analytes to the surfactant-rich phase. In order to separate the phases, the samples were centrifuged at 4000 rpm for 10 min. After the centrifugation, the aqueous phase was removed from the tubes containing the two separated phases. Afterwards, the separated micellar phase was dissolved by an aqueous solution of 1 mol L⁻¹ HNO₃ solution containing 10% (v/v) methanol to a final volume of 2 mL. The reason of adding methanol was to decrease the viscosity and facilitate the introduction of analytes into the nebulizer burner system of the FAAS.

2.3. Real sample preparation

Two different types of standard Reference materials GBW 07603 Tea and GBW 07605 Bush branches and leaves were weighed as 0.20±0.01 g. Solid mushroom samples were dried at 100 °C in an oven for 24 h and ground by using porcelain mortar, blended and sifted with 200 mesh sieves. 0.50±0.01 g portions were weighed precisely. These solid samples were dissolved in a mixture of 6 mL of HNO₃ (65% w/v) and 2 mL of H₂O₂ (30% w/v) at 100 °C for

4 h. Digested samples were diluted appropriately and developed method was applied directly to samples after filtering from quantitative filter paper and pH adjustments. Obtained results were given as the average of at least 4 replicates including standard deviations.

3. RESULTS AND DISCUSSION

3.1. Effect of solution pH

In micelle mediated extraction studies, pH has an impact on solution chemistry and is one of the most important and key parameters for quantitative extraction of metal ions from aqueous solutions. Solution pH strongly effects the complexation between the ligand molecules and metal ions. It also affects the formation of surfactant micelles. In our study the pH optimization experiments were performed between pH 2 to pH 8. The obtained results were given in Figure 1 with standard deviations.

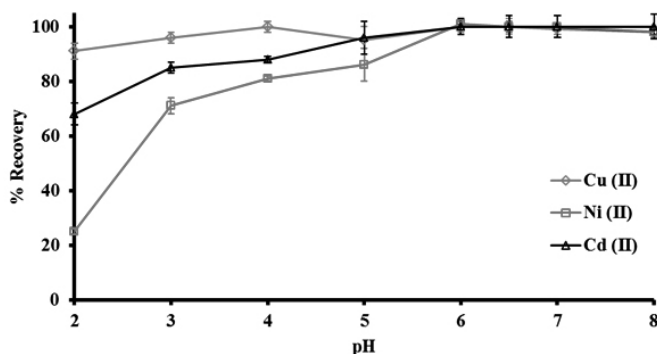


Fig. 1. Effect of pH on the recovery of analyte ions (N=4, DZ concentration: 6×10^{-5} mol L⁻¹, TNP-7 concentration % (w/v): 16×10^{-2} , amounts of analytes: 1 μ g Cu²⁺, 2 μ g Ni²⁺ and 0.8 μ g Cd²⁺, temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL)

According to Figure 1 the recovery values of copper ions were constant and quantitative in all employed pH values but pH 2. Recovery values of nickel ions increased with increasing pH of aqueous media up to pH 6. The recoveries were constant and quantitative for nickel after pH 6. On the other hand, the cadmium recoveries were quantitative between pH 5 and pH 8. As a result, simultaneous quantitative extraction of Cu²⁺, Ni²⁺ and Cd²⁺ ions could be obtained at pH 6.5 and this solution pH was chosen as optimum.

If we consider that, these metal ions were extracted as their dithizone complexes, it is well known that, dithizone forms five-membered stable chelates with Cu²⁺ and Ni²⁺ ions¹⁶. In which, the metal ions are bonded to sulfur atom and coordinately bonded to nitrogen atom of the dithizone.

Multi-dentate ligands play an important role in the stability of metal complexes due to chelate effect. Many quantitative studies have confirmed that metal chelates are more stable than those of related unidentate ligands. Furthermore, five and six-membered chelates have been the most common and the most stable chelates¹⁷. Therefore, higher recovery results of Cu²⁺, Ni²⁺ and Cd²⁺ ions could be gained because of their stable chelates with dithizone.

3.2. Effect of dithizone concentration

Ligand concentration is another important parameter which directly affects the quantitative extraction of metal ions. In our study effect of dithizone concentration was investigated between 0 and 1.0×10^{-4} mol L⁻¹ in 50 mL solution and the results were given in Figure 2 with standard deviations. As shown in Figure 2 the copper extraction was quantitative at 1.2×10^{-5} mol L⁻¹ of dithizone. After then copper recoveries were almost constant, quantitative and curve of the recoveries reached a plateau up to 10×10^{-5} mol L⁻¹ of final ligand concentration. On the other hand, nickel and cadmium recovery values increased with increasing ligand concentration between 0 and 5.0×10^{-5} mol L⁻¹ and no considerable changes were observed on the recovery values of nickel and cadmium after 5.0×10^{-5} mol L⁻¹ dithizone. Therefore 6.0×10^{-5} mol L⁻¹ of final dithizone concentration, quantitatively extracted three metal ions, seemed to be an optimum and applied for all further experiments.

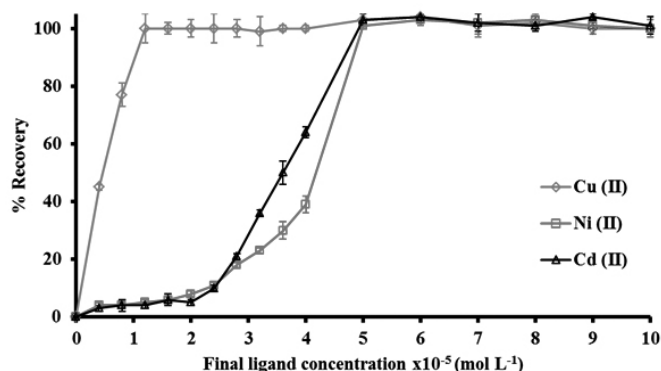


Fig. 2. Effect of DZ concentration on the recovery of analyte ions (N=4, pH: 6.5, TNP-7 concentration % (w/v): 16×10^{-2} , amounts of analytes: 1 μ g Cu²⁺, 2 μ g Ni²⁺ and 0.8 μ g Cd²⁺, temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL)

Although our aim was to preconcentrate and determine the three metal ions together, Fig. 2 clearly indicated that it was also possible to gain selectivity for copper ions by varying the dithizone concentration.

3.3. Surfactant concentration

Another parameter in micelle mediated extraction studies is surfactant concentration that has important effect on quantitative extraction. Lower surfactant concentrations are required to enhance the preconcentration. Effect of surfactant concentration was investigated between 0 and 3.0×10^{-1} % (w/v) in final model solutions. Results were given in Figure 3 with standard deviations. It was shown that recovery values increased up to TNP-7 concentration of 16×10^{-2} % (w/v) in final solution. Metal recoveries were constant at the applied concentrations above 16×10^{-2} % (w/v) of TNP-7 concentration. When a solution heated above the cloud point temperature and if it contains enough micelle monomers, the solution reaches to equilibrium between soluble monomers and insoluble micelles. Constant metal recoveries above 16×10^{-2} % (w/v) of TNP-7 concentration can be attributed to this phenomenon. On the conclusion, the value of 16×10^{-2} % (w/v) of TNP-7 concentration was chosen as optimum surfactant concentration and all following experiments were performed at this concentration.

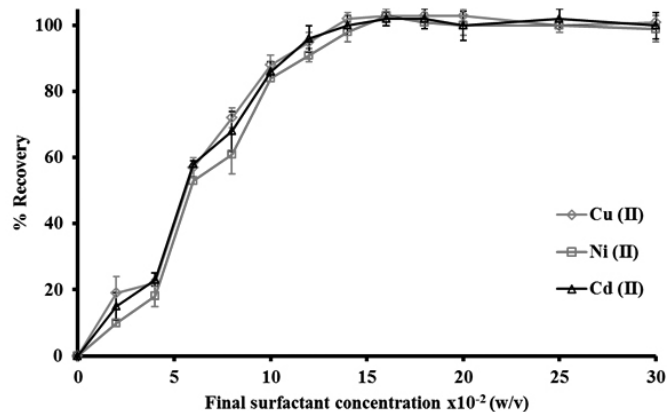


Fig. 3. Effect of surfactant concentration on the recovery of analyte ions (N=4, pH: 6.5, DZ concentration: 6×10^{-5} mol L⁻¹, amounts of analytes: 1 μ g Cu²⁺, 2 μ g Ni²⁺ and 0.8 μ g Cd²⁺, temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL)

3.4. Incubation time, temperature and centrifugation

Optimizations of incubation time and equilibrium temperature are necessary to complete reactions and to perform easy phase separation and preconcentration as efficient as possible¹⁸. In order to obtain complete and effective phase separation, the incubation time and temperature were investigated. The incubation time was investigated from 5 to 30 minutes and equilibrium temperature from 20 to 50 °C. Attained results from these

experiments represented that after 10 minutes of incubation time at 25 °C of equilibrium temperature were sufficient to form adequate micelles. So these values were chosen as optimum.

As Stalikas mentioned in his study, unreasonably high temperatures are not suitable in the micelle mediated extraction method because high temperatures can possibly cause stability problems for chelates and chelating agents and may also decrease the extraction efficiency with possible temperature decrease during the centrifugation and/or phase-separation processes¹⁸. Therefore, it should be avoided that working at high temperatures in micelle mediated extraction experiments. In this point of view our results can be considered as very suitable for micelle mediated extraction.

In order to accelerate phase separation different centrifuge times were performed between 1 and 10 minutes at 4000 rpm. It was observed that no considerable effect was obtained above 5 minutes of centrifugation in term of quantitative extraction. To keep analysis time as short as possible 5 minutes of centrifugation time was selected and all subsequent experiments were performed at 5 minutes of centrifugation.

3.5. Effect of sample volume

In order to obtain maximum and stable analyte signal from the sample solution for higher sample volumes is important to gain higher preconcentration factor which allows analyzing more sample solution at once. Therefore simultaneous extraction of Cu²⁺, Ni²⁺ and Cd²⁺ was investigated for 10, 25 and 50 mL of sample volumes. Effect of sample volume on the recovery of analyte ions were investigated under optimum parameters of the method (N=4, pH: 6.5, DZ concentration: 6x10⁻⁵ mol L⁻¹, TNP-7 concentration % (w/v): 16x10⁻², amounts of analytes: 1 µg Cu²⁺, 2 µg Ni²⁺ and 0.8 µg Cd²⁺, temperature: 25 °C, final volume: 2 mL). The results showed that 102±2, 99±2 and 97±4 % extraction values of Cu were obtained for 10, 25 and 50 of sample volumes. On the other hand the Ni and Cd extraction values were found as 99±1, 97±6, 99±3 and 99±2, 100±2, 101±2 for 10, 25 and 50 mL, respectively.

3.6. Effect of external matrix

In order to find out the effects of some external ions which are possibly exist in water and other real samples, the optimized procedure were subjected at different concentrations to analyte ratio. Results were given in Table 1 with standard deviations.

Table 1 Effect of matrix ions on the recovery of analyte ions (N=4, pH: 6.5, DZ concentration: 6x10⁻⁵ mol L⁻¹, TNP-7 concentration % (w/v): 16x10⁻², amounts of analytes: 1 µg Cu, 2 µg Ni and 0.8 µg Cd, temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL).

Ion	Added as	Amount (µg)	% Recovery		
			Cu	Ni	Cd
Na ⁺	NaNO ₃	10000	98±2	97±2	98±1
K ⁺	KNO ₃	10000	96±4	96±4	95±5
Ca ²⁺	Ca(NO ₃) ₂ .4H ₂ O	1000	100±4	96±2	98±3
Mg ²⁺	Mg(NO ₃) ₂ .6H ₂ O	1000	99±2	81±2	97±1
Cl ⁻	NaCl	10000	98±2	97±2	98±1
NO ₂ ⁻	NaNO ₂	1000	97±2	97±3	98±2
NO ₃ ⁻	NaNO ₃	10000	96±4	96±4	95±5
SO ₄ ²⁻	Na ₂ SO ₄	1000	99±2	100±1	102±2
PO ₄ ³⁻	Na ₃ PO ₄	1000	100±4	96±2	98±3
Fe ³⁺	Fe(NO ₃) ₃ .9H ₂ O	100	101±1	99±2	104±2
Cr ⁶⁺	K ₂ Cr ₂ O ₇	100	104±1	99±1	104±1
Cr ³⁺	Cr(NO ₃) ₃	100	100±2	97±1	103±2
Bi ³⁺	Bi(NO ₃) ₃ .5H ₂ O	50	95±1	96±3	102±1
Al ³⁺	Al(NO ₃) ₃ .9H ₂ O	1000	102±2	98±2	101±3
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	*50/25/25	97±2	97±3	101±3
Pb ²⁺	Pb(NO ₃) ₂	50	99±1	95±3	99±2
Zn ²⁺	Zn(NO ₃) ₂ .6H ₂ O	*50/15/50	97±5	94±4	100±4
Mn ²⁺	Mn(NO ₃) ₂ .4H ₂ O	100	100±3	95±2	99±2
Cu ²⁺	Cu(NO ₃) ₂ .3H ₂ O	20	-	95±1	103±4
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	20	96±2	-	98±1
Cd ²⁺	Cd(NO ₃) ₂ .4H ₂ O	20	97±3	94±1	-

^aMean ± standard deviation ^{*}Different amount for Cu²⁺/Ni²⁺/Cd²⁺

As it is seen from the results in Table 1, the recovery values of Cu²⁺, Ni²⁺ and Cd²⁺ ions were quantitative in the presence of matrix anions and cations.

This stability and selectivity can be explained by the soft-hard acid-base principle (HSAB)¹⁹. The sulfur atom is a soft donor and more prefers soft metal cations than hard metal cations, therefore sulfur atoms of dithizone may showed a potential affinity to form stable complexes with soft and border line metal cations such as Cu²⁺, Ni²⁺, and Cd²⁺. In addition, the nitrogen atoms of dithizone is neither hard nor soft, it lies at the intermediate position and that is true with Cu²⁺, Ni²⁺ and Cd²⁺; because of this fact the dithizone have also shown good affinity towards these metals²⁰. Therefore, these specific tendencies of the nitrogen and sulfur atoms of dithizone, our extraction results were higher for Cu²⁺, Ni²⁺, and Cd²⁺ as expected.

3.7. Effect of internal matrix

The optimized CPE procedure was also investigated in terms of internal matrix to determine any effects of subjected analytes Cu²⁺, Ni²⁺ and Cd²⁺ ions to each other. For this purpose different ratios of these ions were tested in the same solution (described as analyte solution: AS) under optimum conditions and recovery results were given in Table 2.

Table 2 Effect of analyte ions on the recovery of analyte ions (N=4, pH: 6.5, DZ concentration: 6x10⁻⁵ mol L⁻¹, TNP-7 concentration % (w/v): 16x10⁻², temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL).

Internal matrix	Analyte ion (µg)			% Recovery		
	Cu	Ni	Cd	Cu	Ni	Cd
^b AS2	0.25	0.25	0.1	^a 107±3	94±3	107±4
AS3	0.5	0.5	0.2	100±2	97±2	105±5
AS4	1	1	0.4	104±4	105±3	101±6
AS5	1.5	1.5	0.8	103±2	107±4	105±3
AS6	2	2	1.2	99±3	102±1	98±2
AS7	2.5	3	1.6	103±4	106±4	103±2
AS8	3	4	2	99±1	99±3	98±1
AS9	3.5	5	2.4	99±2	98±2	99±2

^aMean ± standard deviation ^bAS: Analyte solution

According to Table 2, nine different AS were examined and satisfactorily recovery values were obtained for all metal ions. This behaviour can be explained by the Irving-Williams theory. The Irving-Williams stability order of bivalent transition metal complexes is Mn²⁺<Fe²⁺<Co²⁺<Ni²⁺<<Cu²⁺²¹. On the other hand, the extraction efficiency values of Cd ions were higher than that of Ni, which can be explained by high affinity of soft sulfur atom toward soft Cd cations. The results obtained in our study are completely correlated with this knowledge.

3.8. SRM, food and water applications

In order to validate and prove the accuracy and precision of the developed extraction method, two different standard reference materials (GBW 07603 Tea and GBW 07605 Bush branches and leaves) were subjected to determine their Cu²⁺, Ni²⁺ and Cd²⁺ contents. The method was also applied to determine copper, nickel and cadmium contents of different mushroom and water samples. Determined metal contents of real samples were also checked with analyte addition technique. Results were given in Table 3 and Table 4 for SRM and real samples, respectively. According to Table 3 obtained results were in accordance with the certified values of two standard reference materials.

Three different water samples which are containing various matrixes were analyzed and the results were given in Table 4. Although the obtained Cu²⁺, Ni²⁺ and Cd²⁺ concentrations of water samples were below quantitation limits, the recovery values proved that the developed method was suitable for their determination.

Table 3 Determination of Cu, Ni and Cd contents of standard reference materials (N=4, pH: 6.5, DZ concentration: 6×10^{-5} mol L⁻¹, TNP-7 concentration % (w/v): 16×10^{-2} , temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL).

SRM	Cu			Ni			Cd		
	Certified value ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	% Recovery	Certified value ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	% Recovery	Certified value ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	% Recovery
GBW 07603	6.6	^a 6.4±0.1	96±1	1.7	1.7±0.1	99±4	0.38	^b BDL	^c ND
GBW 07605	17.3	17.1±0.8	99±4	4.60	4.8±0.2	104±4	0.057	BDL	ND

^aMean±standard deviation ^bBelow detection limit ^cNot determined

Table 4 Determination of Cu, Ni and Cd contents of mushroom and water samples with analyte addition (N=4, pH: 6.5, DZ concentration: 6×10^{-5} mol L⁻¹, TNP-7 concentration % (w/v): 16×10^{-2} , temperature: 25 °C, sample volume: 50 mL, final volume: 2 mL).

Sample	Added (μg)			Found (μg)			% Recovery			Content ($\mu\text{g g}^{-1}$)		
	Cu	Ni	Cd	Cu	Ni	Cd	Cu	Ni	Cd	Cu	Ni	Cd
Mushroom A	-	-	-	^a 5.68±0.09	1.68±0.07	^b BDL	-	-	-	34.08±0.53	10.05±0.40	^c ND
	0.25	0.50	0.20	5.90±0.18	2.14±0.06	0.29±0.02	99±3	99±1	96±4	-	-	-
	0.50	1.00	0.40	6.11±0.06	2.53±0.03	0.46±0.02	99±2	95±3	98±3	-	-	-
Mushroom T	-	-	-	6.05±0.12	0.57±0.01	0.53±0.04	-	-	-	35.98±0.70	3.38±0.07	3.11±0.23
	0.25	0.50	0.20	6.31±0.21	1.01±0.10	0.69±0.05	98±5	99±3	95±2	-	-	-
	0.50	1.00	0.40	6.49±0.28	1.32±0.03	0.90±0.05	96±6	94±2	98±1	-	-	-
Mushroom B	-	-	-	3.36±0.06	0.44±0.01	0.45±0.02	-	-	-	20.09±0.34	2.65±0.09	2.69±0.10
	0.25	0.50	0.20	3.74±0.11	0.90±0.03	0.65±0.01	103±2	95±2	99±2	-	-	-
	0.50	1.00	0.40	3.92±0.17	1.24±0.02	0.83±0.04	95±4	96±1	98±4	-	-	-
Tap water	-	-	-	^b BDL	^b BDL	^b BDL	-	-	-	^c ND	^c ND	^c ND
	0.50	1.0	0.40	0.57±0.01	0.97±0.01	0.41±0.01	106±1	97±1	102±1	-	-	-
	1.00	2.0	0.80	1.02±0.04	1.88±0.04	0.75±0.02	102±4	94±2	94±2	-	-	-
Lake water	-	-	-	^b BDL	^b BDL	^b BDL	-	-	-	^c ND	^c ND	^c ND
	0.50	1.0	0.40	0.54±0.02	1.01±0.03	0.40±0.02	108±4	101±3	101±4	-	-	-
	1.00	2.0	0.80	0.98±0.02	1.96±0.02	0.75±0.01	98±2	98±1	94±1	-	-	-
Waste water	-	-	-	^b BDL	^b BDL	^b BDL	-	-	-	^c ND	^c ND	^c ND
	0.50	1.00	0.40	0.56±0.01	1.01±0.01	0.43±0.02	104±2	101±1	109±4	-	-	-
	1.00	2.00	0.80	1.01±0.02	1.89±0.03	0.79±0.02	101±2	94±1	99±2	-	-	-

^aMean±standard deviation ^bBelow detection limit ^cNot determined

The copper levels of mushrooms were determined between 20.04 $\mu\text{g g}^{-1}$ and 34.08 $\mu\text{g g}^{-1}$. Nickel and cadmium contents of mushroom samples were determined between 2.65-10.05 $\mu\text{g g}^{-1}$ and 2.69-3.11 $\mu\text{g g}^{-1}$, respectively. Cu^{2+} , Ni^{2+} and Cd^{2+} levels of mushroom samples were also checked with analyte addition.

3.9. Analytical figures of method

The results of regression equations are obtained from the absorbance

of three metal ions after applying the CPE procedure. The limit of detection (LOD) of the method was calculated by adding the 3 times the standard deviation (σ) for 21 repetitive of blank solutions to average of the absorbance and dividing it to slope of calibration graph ($3\sigma/\text{slope of calibration graph}$). The limit of quantification (LOQ) was calculated similar to LOD in which 10 times of the standard deviation was taken. Analytical parameters were summarized in Table 5.

Table 5 Analytical characteristics of the method.

Analytical parameters	Cu	Ni	Cd
LOD ($\mu\text{g L}^{-1}$)	0.5	1.8	2.0
LOQ ($\mu\text{g L}^{-1}$)	1.3	2.9	4.8
LDR ($\mu\text{g mL}^{-1}$)	0.125-2	0.125-2.5	0.05-1.4
^y Regression equation	A=0.1439C+0.0049	A=0.0969C+0.0081	A=0.2457C+0.0119
^y Correlation coefficient	0.9990	0.9964	0.9980
Preconcentration factor	25	25	25
% RSD	5	7	6
^t Calibration curve	A=0.1794C+0.0045	A=0.1264C-0.0014	A=0.2996C-0.0019
^t Correlation coefficient	0.9991	0.9996	0.9994

LOD: Limit of detection LOQ: Limit of quantitation

LDR: Linear dynamic ranges RSD: Relative standard deviation
^yObtained with preconcentration
^tObtained without preconcentration

Developed method permits a preconcentration factor of 25 and LOD values were 0.5, 1.8 and 2.0 $\mu\text{g L}^{-1}$ for Cu^{2+} , Ni^{2+} and Cd^{2+} respectively. A comparison of the developed method with recent studies was given in Table 6. The developed method was comparable with other studies according to characteristics of the method (temperature, LOD and PF).

Table 6 Some recent simultaneous micelle mediated cloud point extraction studies for determination of multi metal.

Detection system	Surfactant	Determined metal	Ligand	Temperature, (°C)	LOD, ($\mu\text{g L}^{-1}$)	% RSD	LDR, ($\mu\text{g mL}^{-1}$)	PF	Reference
F-AAS	Triton X-114	Cd, Pb	DDTP	40	0.62-2.86	1.39-1.67	0.003-0.46	25	22
F-AAS	Triton X-114	Cd, Ni	Dithizone	40	0.31-1.2	2.3-2.4	0.001-0.18	39	23
F-AAS	Tween 80	Cd, Cr, Pb, Cu, Ni, Bi	Ligandless	60	0.4-7.2	6.0	0.2-12	10	24
ICP-OES	Triton X-114	Cd, Co, Ni, Pb, Zn, Cu	8-HQ	55	0.01-0.34	4.19-5.57	0.04-4	9.95	25
F-AAS	Triton X-114	Cd, Ni, Zn	PAN	60	0.37-2.6	2.0-2.6	0.005-0.16	30	26
F-AAS	Triton X-114	Cu, Pb, Zn	TAN	40	9.5×10^{-3} - 1.1×10^{-3}	1.5-3.5	9.5×10^{-5} - 0.16	55.6	27
F-AAS	Triton X-114	Pb, Co, Cu	1-PTSC	50	0.67-3.42	1.7-4.8	0.25-10	25	28
F-AAS	Triton X-114	Cu, Zn, Fe, Ni	PHBI	50	1.8-2.8	2.0-3.6	0.02-0.26	30	29
F-AAS	Triton X-114	Cu, Ni, Zn, Fe	IYPMI	50	1.1-2.8	2.1-3.6	0.01-0.3	30	30
F-AAS	Triton X-114	Fe, Co, Ni	APDC	70	5-19	1.71-4.76	0.02-0.35	20	31
F-AAS	Triton X-114	Cu, Fe, Zn, Ni	BIYPYBI	50	1.0-2.2	0.6-1.4	0.01-0.25	30	32
F-AAS	Triton X-114	Ag, Pd	BIMPI	55	10-25	1.85-2.70	0.028-0.72	28	33
F-AAS	Tergitol NP7	Cu, Ni, Cd	Dithizone	25	0.5-2.0	5-7	0.125-2.5	25	Present study

LOD: Limit of detection RSD: Relative standard deviation PF: Preconcentration factor LDR: Linear dynamic range

AAS: Atomic absorption spectrometer F: Flame ICP-OES: Inductively coupled plasma optical emission spectrometer

PAN: Pridyl-azo-naphthol DDTP: Diethyldithiophosphate APDC: Ammonium pyrrolidine dithio carbamate Dithizone: Diphenyl dithio carbazone
8-HQ: 8-hydroxyquinoline TAN: 1-(2-thiazolylazo)-2-naphthol 1-PTSC: 1-Phenylthiosemicarbazide PHBI: 2-phenyl-1H-benzo[d]imidazole
IYPMI: 3-((indolin-3-yl)(phenyl)methyl)indoline BIYPYBI: 2-(6-(1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1H-benzo[d]imidazole
BIMPI: 2-(2-((1H-benzo[d]imidazole-2-yl)methoxy)phenoxy)methyl-1H-benzo[d]imidazole

4. CONCLUSION

It was proved that CPE-FAAS by using Tergitol[®] type NP-7 surfactant is a suitable technique for the simultaneous determination of copper, nickel and cadmium. Dithizone formed stable metal chelates with the stability order of $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. The cloud point temperature of the surfactant used was very low compared to other non-ionic surfactants. So, remarkable advantages could be gained on the determination of multi element analysis. Therefore, preconcentration and determination of Cu^{2+} , Ni^{2+} and Cd^{2+} in real samples could be achieved with lower incubation time and cloud point temperature. This improved the method by means of low running costs, energy consuming, fastness and practical.

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