

# Application of Flotation and Spectrophotometric Detection for Preconcentration and Separation of Trace Amounts of Cadmium Ion Using a New Ligand 3-((1H indole-3-yl) (4-Cyano Phenyl) Methyl) 1H Indole (ICPMI) in Real Samples

Gerçek Numunelerde Yeni Bir Ligand Olan 3-((1H İndol-3-yl) (4-Siyano Fenil) Metil) 1H İndol Kullanarak Eser Miktarda Kadmiyum İyonunun Ön Deriştirme ve Ayrılması için Spektrofotometrik Analiz ve Flotasyon Uygulaması

Research Article

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## ABSTRACT

An efficient flotation method based on the combination of flame atomic absorption spectrometry (FAAS) and separation and preconcentration step for determination of Cd<sup>2+</sup> ions in various real samples by the possibility of applying Ligand 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI), as a new collector was studied. The influence of pH, amount of ICPMI as collector, sample matrix, type and amount of eluting agent, type and amount of surfactant as floating agent, ionic strength and air flow rates i.e. variables affecting the efficiency of the extraction system was evaluated. It is ascertained that cadmium ion separated simultaneously from matrix in the presence of 0.012 mM ligand, 0.025% (w/v) of sodium dodecyl sulfate (SDS) and pH 9.0±0.1. These ions can be eluted quantitatively with 0.5 mL of 1M HNO<sub>3</sub> in methanol linear range of the determination is between 0.02-2.2 µg mL<sup>-1</sup> for Cd<sup>2+</sup> with a detection limit for Cd<sup>2+</sup> was 1.9 µg mL<sup>-1</sup> respectively. The method has been successfully applied for determination of trace amounts of cadmium ion in radiology wastewater, amalgam, natural water and blood samples.

## Key Words

Trace, Ion flotation, sodium dodecylsulfate, Flame atomic absorption spectrometry.

## ÖZ

Alev atomik absorpsiyon spektrometrisine dayanan etkin bir flotasyon yöntemiyle ayırım ve ön deriştirme adımları toplayıcı olarak ligand 3-((1H-indol-3-il) (4-Siyano fenil) metil) 1H-indol (ICPMI) ile çeşitli gerçek örneklerde Cd<sup>2+</sup> iyonlarının tayini incelenmiştir. pH, ICPMI miktarı, numune matrisi, elüsyon maddesinin türü ve miktarı, yüzey aktif maddenin türü ve miktarı, iyonik kuvvet, hava akış oranı, yani ekstraksiyon sisteminin verimliliğini etkileyen değişkenler değerlendirildi. Kadmiyum iyonunun 0.012 mM ligandı, %0.025 (w/v) sodyum dodesil sülfat (SDS) ve pH 9.0±0.1 varlığında eşzamanlı olarak matristen ayrıldığı kesin olarak belirlendi. Bu iyonlar, metanolde 1M HNO<sub>3</sub>'ün 0.5 mL si ile nicel olarak, Cd<sup>2+</sup> için 0.02-2.2 µg mL<sup>-1</sup> arasında ve Cd<sup>2+</sup> için saptama limiti 1.9 µg mL<sup>-1</sup> olan doğrusal aralıklarla ayrılabilir. Yöntem, radyoloji atık suyu, amalgam, doğal su ve kan numuneleri örneklerinde az miktarda kadmiyum iyonu tayini için başarıyla uygulanmıştır.

## Anahtar Kelimeler

İz, iyon flotasyonu, sodyum dodesilsülfat, alev atomik absorpsiyon spektrometresi.

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## INTRODUCTION

Study of water and food pollution by heavy metals has been of great interest. Heavy metals such as cadmium (Cd) can be harmful to human health even in very low concentrations, as well as being highly toxic and non-degradable. International agency for research on cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans [1,2]. Cadmium is efficiently retained in the kidney (half-time of 10-30 years) and the concentration is proportional to that in urine [3]. Recent data indicate that adverse health effects of cadmium exposure may occur at lower exposure level than previously anticipated [4]. Due to high toxicity of cadmium, a sensitive and accurate analytical method is required for measuring and determination of trace amount of cadmium in the samples.

Flame atomic absorption spectrometry (FAAS) [5,6], is frequently employed as an analytical technique due to its simplicity and low cost. Additionally, it is fast, accurate, and precise. On the other hand, insufficient sensitivity or matrix interferences limit the applications of FAAS. These difficulties have been eliminated by various separation and preconcentration techniques. Solvent extraction [7], precipitation/coprecipitation [8], cloud point extraction [9], solid phase extraction (SPE) [10], electroanalytical technique [11] and flotation [12]. Some of the extraction methods suffer from inconveniences such as, lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi stage, lower enrichment factor and consumption of organic harmful solvents which can be overcome by replacement of filtration or centrifugation by flotation [13-15]. Flotation as a preconcentration methods include flotation, macro flotation, colloidal flotation, ion flotation and precipitate flotation. Precipitate and adsorbing colloid flotation are processes that, together with ion flotation, possess some advantages for treating large volumes of wastewater solutions. Precipitate flotation requires precipitation of the metal species in preparation for subsequent flotation [16,17].

The small amount of a surfactant and the tiny air bubbles require to perform the proper

flotation prevent serious contamination risks, which could be manifested by the high blank value. Many factors influence to perform a proper flotation, but an important role has the collector with its colloid nature [18-22]. According to our knowledge there is still not reported any method in the literature, based on the simultaneous flotation of transition and heavy metal ions using Schiff's bases ligand. Therefore, in detail it was decided to develop an efficient method for the extraction and preconcentration of trace amounts of cadmium ion from aqueous media using ligand 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI) [23] and determination by FAAS.

## EXPERIMENTAL

### Instruments

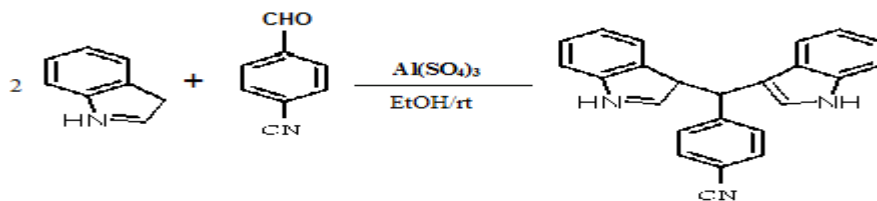
A Shimadzu atomic absorption spectrophotometer (model 680) was used for determining concentration of Cd<sup>2+</sup> at 228.8 nm. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. The pH was adjusted and measured using pH/Ion meter model 691 (Metrohm, Switzerland, Swiss).

### Reagents

Acids, bases and nitrate salt of all metal ions under study were of the highest purity available from Merck Darmstadt (Germany) and were used as received. Double-distilled deionized water was used throughout. The pH adjustment was done by the addition of dilute HNO<sub>3</sub> or/and NaCl to sample to obtain the desired pH sample solution. The Ligand 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI) was synthesized according to literature [23].

### Synthesis of 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI)

ICPMI was synthesized according to a procedure in the literature [39]. A mixture of indole 1 (2 mmol), 3-cyanobenzaldehyde (1 mmol), and aluminum hydrogen sulfate (1mmol) in ethanol (4 ml) was magnetically stirred at room temperature. After 4 h the reaction mixture was filtered. The residue was washed with EtOH (2×4 ml). Water (25ml) was then added to the filtrate and the precipitate was filtered. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-



**Figure 1.** Ligand 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI).

hexane (10:90)] to give pure 3-((1H indole-3-yl) (4-cyano phenyl) methyl) 1H indole (ICPMI) in 90% yield.

### Flotation-Separation Procedure

A separation funnel with sidelong tube was used for flotation-separation. The separation funnels a sample solution containing  $0.2 \mu\text{g mL}^{-1}$  of each ion,  $0.5 \text{ mL } 1.0 \text{ M}$  of  $\text{HNO}_3$  solution.  $1.0 \text{ mL}$  of  $0.06\%$  (w/w) solution of SDS and  $0.35 \text{ mL}$  of  $10^{-3} \text{ M}$  of ICPMI and  $6 \text{ mL}$  of saturated  $\text{KNO}_3$  were added, the pH of medium was carefully adjusted to  $9.0 \pm 0.1$  with nitric acid or sodium hydroxide solution. The mixture was diluted to  $25 \text{ mL}$  and after stirring for  $20 \text{ min}$ . then an air stream ( $25 \text{ mL min}^{-1}$ ) was kept flowing for  $2\text{-}4 \text{ min}$  to raise the foam layer to the water surface. A foamy layer was thus obtained and the aqueous solution in the cell became clear. Then the aqueous solution in the cell became clear was ousted of separation funnel and the foam layer was dissolved in  $0.5 \text{ mL } 1.0 \text{ M } \text{HNO}_3$  in methanol and then the metal ions content was readily evaluated by FAAS.

### Application to Real Samples

Real samples including blood samples were treated as described previously [24]. Then the Test Procedure described above was applied. For the application of the present procedure to amalgam alloy, an accurately weighed  $0.4 \text{ g}$  portion of each amalgam alloy sample was digested as described previously [25,26]. and dissolved in the smallest volume of water, and the solution was transferred to a  $100 \text{ mL}$  volumetric flask by adjustment of the pH of the solution to the desired value; then the Test Procedure described above was carried out. The waste radiographic samples were prepared for the measurement of their cadmium content as follows. To  $20 \text{ mL}$  sample were added about  $10 \text{ mL } 3 \text{ M}$  nitric acid and  $10 \text{ mL}$  water. The solution was boiled until its volume was reduced to  $20 \text{ mL}$ . The resulting solution was neutralized with NaOH

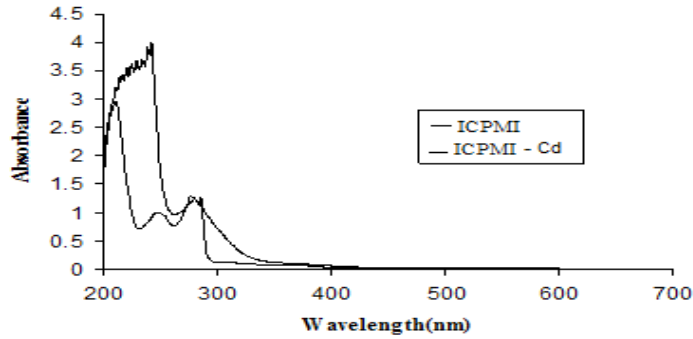
solution to the desired pH value and filtered. The filtrate and washings were diluted to  $50 \text{ mL}$  in a volumetric flask, and then the Test Procedure described above was applied.

### RESULTS and DISCUSSION

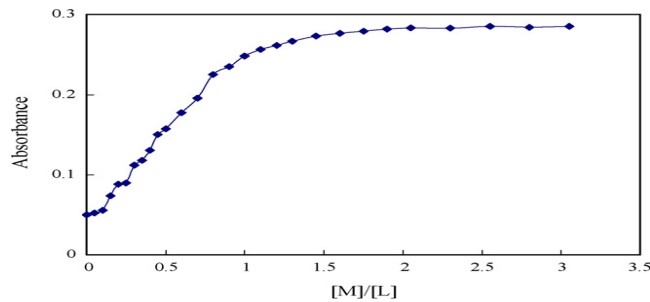
The aim of this work was to develop a simple, sensitive and available method for the pre-concentration and determination of trace amounts of  $\text{Cd}^{2+}$  ion in various real samples using flame atomic absorption spectrometry coupled with flotation. In this regard, the influence of various effective parameters including, pH, surfactant and ICPMI concentrations, as well as the effect of electrolyte on absorbance, were optimized. The complexation study yields important information about the interaction between the ligand and metal ions. Recently, we have used the spectrophotometric method for this purpose [27,28], before using ICPMI for the flotation of the metal ions.

### Spectrophotometric Titrations

Standard stock solutions of ligands ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) and metal ion ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) were prepared by dissolving appropriate and exactly weighed in pre-calibrated  $25.0 \text{ mL}$  volumetric flasks and diluted to the mark with acetonitrile. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution ( $7.41 \times 10^{-5} \text{ mol L}^{-1}$ ) was carried out by the addition of microliter amounts of a concentrated standard solution of the metal ion in acetonitrile ( $1.0 \times 10^3 \text{ mol L}^{-1}$ ) using a pre-calibrated micropipette, followed by absorbance intensity reading at  $25.0^\circ\text{C}$  at the related maximum wavelength. Since the volume of titrant added during titration was negligible (at the most  $0.05 \text{ mL}$ ) as compared with the initial volume of the ligands ( $2.6 \text{ mL}$ ), no volume correction was carried out [29,30].



**Figure 2.** Absorption spectra of ICPMI-Cd complex. Conditions: 0.06% (w/v) SDS, 0.35 mM ICPMI and  $0.2 \mu\text{g mL}^{-1}$  cadmium ion.



**Figure 3.** UV-visible spectra for titration of L ( $7.41 \times 10^{-5} \text{ mol L}^{-1}$ ) with  $\text{Cd}^{2+}$  ( $1.00 \times 10^{-3} \text{ mol L}^{-1}$ ) in MeOH ( $T=25^\circ\text{C}$  and  $I = 0.05 \text{ mol L}^{-1}$ ). (a) The molar ratio plot in  $\lambda_{\text{max}}=263$  (b) The corresponding computer fitted curve of absorbance vs.  $[\text{Cd}^{2+}/\text{L}]$ .

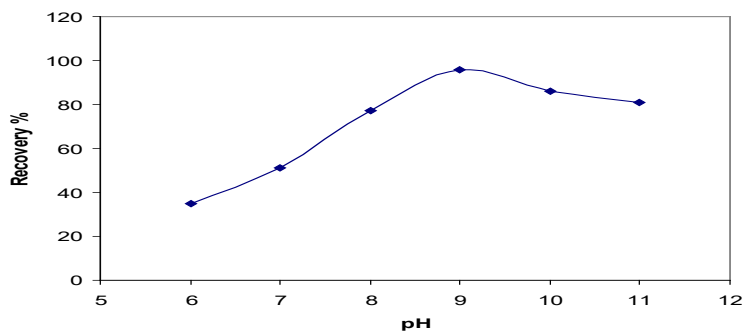
### Influence of pH

The formation of the metal-chelate and its chemical stability are two important factors influencing flotation. The pH plays a unique role in metal-chelate formation and subsequent extraction, proving to be the main parameter for flotation. The extraction efficiency is dependent on the pH at which complex formation occurs [31-33]. Thus, a set of similar experiments in the pH range 6.0-11.0 was conducted according to the described procedure described in the experimental section with respective results illustrated in Figure 4. The maximum sensitivity by flotation was obtained at  $\text{pH } 9.0 \pm 0.1$ . In more acidic solutions, deterioration of the signal occurs due to protonation of ICPMI, while at  $\text{pH} > 9.0 \pm 0.1$ , the signal decreases and

recovery is reduced due to precipitation of  $\text{Cd}^{2+}$  ion in the form of hydroxides or ternary complexes. Consequently,  $\text{pH} = 9.0 \pm 0.1$ , was selected for the subsequent studies.

### Influence of ICPMI Concentration

The evaluation of the concentration of complexing agent on the recoveries of the analytes in the floated layer was performed in the range of  $1.0 \times 10^{-4}$  to  $3.5 \times 10^{-3} \text{ mol/L}$  of ICPMI. At  $\text{pH} = 9.0 \pm 0.1$ , 25 mL of a sample solution containing  $3.5 \times 10^{-4} \text{ mol/L}$  of each of the metal ions and 4 mL the perfect flotation separation of the metal ions was achieved at ICPMI concentration greater than  $3.5 \times 10^{-4} \text{ mol/L}$  Figure 5. Thus, the solution of ICPMI with concentration of  $3.5 \times 10^{-4} \text{ mol/L}$  was used for subsequent



**Figure 4.** Effect of pH on ions recoveries.

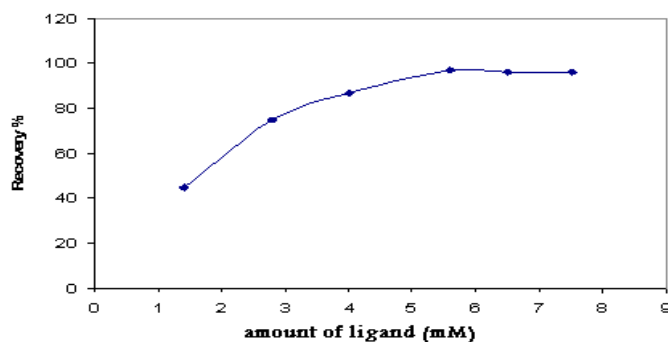


Figure 5. Effect of ICPMI on ions recoveries.

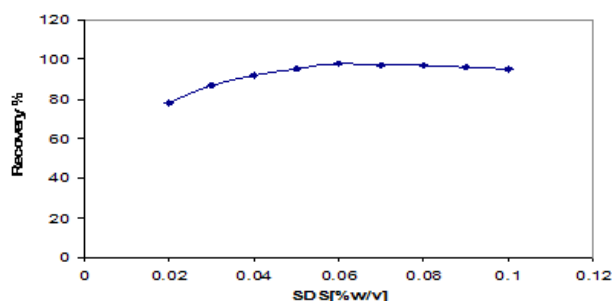


Figure 6. Effect of SDS on ions recoveries.

experiments. Since the separation efficiency remained constant in the presence of excess amounts of ICPMI, this ligand could easily be used for investigation of the samples containing unknown amounts of the analytes.

### Selection of Surfactant

To select the most effective tenside among several cationic, anionic and non-ionic surfactants, a number of tests under previously optimized conditions were carried out and respective results are presented in Table1. The flotation by use of TX-100 and TX-114 was also ineffective [34]. The anionic surfactants were more effective. The ions flotation recoveries obtained by SDS within the optimal pH range  $9.0 \pm 0.1$ , were greater than 98.5-99.0%. The anionic surfactant SDS was chosen

**Table1.** Effect of type of surfactant on sensitivity for  $0.2 \mu\text{g mL}^{-1}$  of interest ion, pH  $9.0 \pm 0.1$ , ICPMI ( $3.5 \times 10^{-4} \text{ mol/L}$ ) and 0.06 % (w/v) of each surfactant.

Surfactant	Cd %
Triton X-114	48.7
SDS	98.6
Triton X-100	32.0
No surfactant	25.9

because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost.

The flotation efficiency was evaluated using SDS concentrations ranging from 0.02% to 0.1% (w/v). The highest cadmium ion recovery was obtained with 0.06% (w/v) SDS. By decreasing the surfactant concentration to 0.06% (w/v) the recovery was reduced. The cadmium ion recovery also decreased for a higher SDS concentration (0.06% w/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [35-37]. At lower SDS concentrations (below 0.06% w/v), the pre-concentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex and float the complex [38]. Since, 0.06% (w/v) of SDS showed the highest cadmium ion recovery; a surfactant concentration of 0.06% (w/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration.

### Effect of Ionic Strength

It is known that ionic strength of the solution is one of the effective factors in flotation. In this work, the effect of  $\text{KNO}_3$  salt as an electrolyte in the range  $0.01\text{-}0.5\text{ mol L}^{-1}$  on the process was investigated [39]. It is observed that increasing concentration of salt to  $0.1\text{ M}$  exerts no effect on the process, but higher concentrations caused a decrease in absorbance of extracted surfactant-rich phase. This effect might be explained by the additional surface charge when the salt concentration is very high.

### Calibration, Precision and Detection Limits

Calibration graphs were obtained by pre-concentration of  $25\text{ mL}$  of several solutions under optimum conditions, containing various concentrations of each analyte, with the process performed according to the General procedure section where the absorbance of the final solution was measured by AAS. A linear relationship between the measured absorbance and concentration of  $\text{Cd}^{2+}$  ion in the Linear Range  $0.02\text{-}2.0\mu\text{g mL}^{-1}$  was obtained [40,41]. Figure 7. and Table 2. shows the calibration parameters for the proposed flotation method including the linear ranges, the relative standard deviation obtained for two analyte samples subjected to the complete procedure, volume ratio and the limit of detection. Also, a calibration graph was obtained without pre-concentration in order to calculate the enrichment factor. The enrichment factor was calculated as the ratio of the slopes of the calibration curve with and without pre-concentration, and Detection limit for  $\text{Cd}^{2+}$  ion was  $1.9\text{ (ng mL}^{-1}\text{)}$ , respectively.

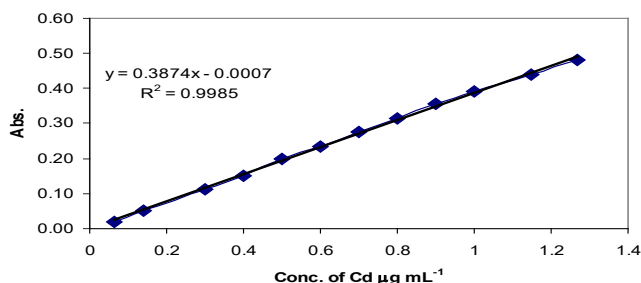


Figure 7. Calibration Curve by dithizone method for  $\text{Cd}^{2+}$  ion.

Table 2. Specification of presented method at optimum conditions for each element.

Parameters	Cd
Linear Range ( $\mu\text{g mL}^{-1}$ )	0/2-02/0
Correlation Coefficient	9985/0
Detection Limit ( $\mu\text{g}\cdot\text{mL}^{-1}$ ) (n =10)	9/1
Preconcentration factor	37
RSD % (n =5)	3/1
Recovery %	99

### Flotation Mechanism

There are in fact two main types of interactions involved in the process of flotation, namely physical and electrostatic interactions [42-44]. The predominance of the electrostatic mechanism is mainly governed by such important factors as the size and charge of ionic species involved, the presence of electronegative atoms capable of forming hydrogen bonds in the ligand structure, and charged sites on the precipitates. Based on the existence and observation of some experimental factors in the present work, it seems reasonable to assume the redominance of an electrostatic mechanism for the proposed flotation system. Which possess high tendencies for forming H-bonds with the surfactant; the inability of Triton SDS as a ionic surfactant for flotation of the metal ions complexes involved.

### Interference Study

The accuracy and reliability of this method was evaluated by comparing the results obtained for the same samples by an FAAS method. The results estimated by FAAS and spectrophotometry are shown in Table 3. The results estimated by spectrophotometry are much less as compare to results obtain by FAAS. It may be attributed to the interference of foreign ions in the determination of cadmium. The interfering ions. These ions may interfere with cadmium(II). The tolerated limits for the ions assayed are shown in Table 4, (was relative errors less than 5%). As can be seen, the proposed method is highly selective.

### Real Samples-Evaluation of Method

The proposed method was applied for the determination of  $\text{Cd}^{2+}$  ion by the standard addition technique in wastewater and tap water samples.

**Table 3.** Effects of the matrix ions on the recoveries of the examined metal ions (N=5).

Ions	Added As	Tolerance Limit, mg L <sup>-1</sup>
Cl <sup>-</sup> , K <sup>+</sup> , Na <sup>+</sup> ,	KCl, NaCl, MgCl <sub>2</sub> ,	800
Zn <sup>2+</sup> , Ba <sup>2+</sup>	Nitrate salts	200
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	800
Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>3+</sup> , Hg <sup>2+</sup>	Nitrate salts	500
Ca <sup>2+</sup> , Mg <sup>2+</sup>	Nitrate salts	50
Ti <sup>+</sup> , Al <sup>3+</sup> ,	Nitrate salts	150
HCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	700

including well wastewater and tap water samples (Tables 4 and 5). The results of in natural water and blood samples. as mentioned in the Experimental section are summarized in Tables 4 and 5. Notably, the determination of Cd<sup>2+</sup> in radiology wastewater, amalgam, natural water and blood samples. is remarkably accurate by the proposed method. The results of the determination of Cd<sup>2+</sup> in the in radiology wastewater, amalgam, natural water and blood samples. as mentioned in the experimental section are listed in Tables 4 and 5.

## CONCLUSION

The flotation of Cd<sup>2+</sup> ion with ICPMI into the phase of cationic surfactant SDS has been investigated. The sensitivity, metrological characteristics, ecological safety, simplicity and convenience of the suggested procedure are superior with respect to the methods based on the extraction with organic solvents. The present method has following advantages over reported methods: (a) synthesized organic reagent could be synthesized in our laboratory with high efficiency and low cost. This reagent is distinct in terms of sensitivity, selectivity towards metal ions. (b) Optimum volume of the eluting solution and low consumption of chemical reagents obtained by using the present methodology permitted to design an extraction strategy that posses one of the following advantages presenting robustness, low cost, low RSD and LOD good extraction efficiency and lower toxicity than those previously reported in literature the pre-concentration factor is relatively.

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**Table 4.** Recovery of trace elements from radiology wastewater and natural water samples after application of presented flotation procedure (N=3).

Ion	Added, µg L <sup>-1</sup>	Found, µg L <sup>-1</sup>	RSD %	Recovery %
radiology wastewater				
Cd	0	9.7	1.4	---
	25	25.0	1.1	100.4
natural water				
Cd	0	0.87	1.4	---
	25	1.1	1.0	102.3

**Table 5.** Recovery of trace elements from amalgam and blood samples after application of presented flotation procedure (N=3).

Ion	Added, µg L <sup>-1</sup>	Found, µg L <sup>-1</sup>	RSD %	Recovery %
amalgam				
Cd	0	4.5	1.3	---
	25	20.0	1.5	103.0
blood				
Cd	0	2.3	1.4	---
	25	17.1	1.6	98.0

## References

1. C. Baird, Environmental Chemistry, 2nd edition, W.H. Freeman and Company, New York, 1999.
2. F. Ansar Khameneh, M. Baghdadi, Z. Monsef Khoshheha, Determination of trace amount of cadmium in real water and baby food samples by microinjection flame atomic absorption spectrometry after cloud point extraction using selective synthesis ligand, *J. Advan. Chem.*, 7 (2014) 1420-1433.
3. J. Thompson, J. Bannigan, Cadmium: toxic effects on the reproductive system and the embryo, *Reprod. Toxicol.*, 25 (2008) 304-315.
4. L. Jarup, A. Akesson, Current status of cadmium as an environmental health problem, *Toxicol. Appl. Pharmacol.*, 238 (2009) 201-208.
5. A.A. Gouda, A new coprecipitation method without carrier element for separation and preconcentration of some metal ions at trace levels in water and food samples, *Talanta*, 146 (2016) 435-441.
6. Z. Bahadır, V. N. Bulut, D. Ozdes, C. Duran, H. Bektas, M. Soylyak, Separation and preconcentration of lead, chromium and copper by using with the combination coprecipitation-flame atomic absorption spectrometric determination, *J. Ind. Eng. Chem.*, 20 (2014) 1030-1034.
7. H. Kalkan, M. Kaplan, S. Orman, Revegetation of Abandoned Sulphur Flotation Waste in Kecioborlu, Isparta/Turkey: Heavy Metals Concentrations of Growing Media and Agropyron elongatum Grass, *Not Bot Horti Agrobo*, 42 (2014) 340-346.
8. M. Behbahani, P. G. Hassanlou, M. M. Amini, F. Omid, A. Esrafil, M. Farzadkia, A. Bagheri, Application of solvent-assisted dispersive solid phase extraction as a new, fast, simple and reliable preconcentration and trace detection of lead and cadmium ions in fruit and water samples, *Food Chem.*, 187 (2015) 82-88.
9. M. Ghaedi, K. Mortazavi, M. Jamshidi, M. Roosta, B. Karami, Oxidized multiwalled carbon nanotubes modified with 2-(2-hydroxy-5-nitrophenyl)-4,5-diphenyl imidazole for solid phase extraction and preconcentration of some metal ions, *Toxicol. Environ. Chem.*, 94 (2012) 846-859.
10. A. Shokrollahi, H.E. Haghghi, E. Niknam, K. Niknam, Application of cloud point preconcentration and flame atomic absorption spectrometry for the determination of cadmium and zinc ions in urine, blood serum and water samples, *Quím. Nova São Paul*, 36 (2013) 273-283.
11. M. Soylyak, E. Yilmaz, Determination of Cadmium in Fruit and Vegetables by Ionic Liquid Magnetic Microextraction and Flame Atomic Absorption Spectrometry, *Anal. Lett.*, 48 (2015) 464-476.
12. M.H. Salmani, M. Davoodi, M.H. Ehrampoush, M. Taghi Ghaneian, M.H. Fallahzadah, Removal of cadmium (II) from simulated wastewater by ion flotation technique, *J. Environ. Health. Sci. Eng.*, 10 (2013) 1186-1197.
13. M. Ghaedi, K. Niknam, S.N. Kokhdan, M. Soylyak, Combination of flotation and flame atomic absorption spectrometry for determination, preconcentration and separation of trace amounts of metal ions in biological samples, *Human and Experimental Toxicology*, 32 (2013) 504-512.
14. M.F. Del, V. Gonzalez, I. Garcia, J.A., Sanchez, Effect of organic and inorganic residues on the solubility of trace elements and phytotoxicity of mining waste, *Fresenius Environmental Bulletin*, 19 (2010) 2071-2076.
15. Y.A. Zolotov, N.M. Kuzmin, preconcentration of trace elements, Elsevier, Amsterdam, 1990.
16. M. Caballero, R. Cela, J. A. Pérez-Bustamante, Analytical applications of some flotation techniques a review, *Talanta*, 37 (1990) 275.
17. L.K. Wang, Y.T. Hung, N.K. Shammass, Advanced physicochemical treatment processes, Humana Press., (2006) 89.
18. M. Ghaedi, A. Shokrollahi, M. Montazerzohori, F. Mahel, M. Soylyak, Development of a flotation method for preconcentration-separation of trace amounts of some metal ions in plant tissues prior to their FAAS determinations, *Quim. Nova*, 33 (2010) 404-410.
19. Y.S. Kim, Y.S. Choi, W. Lee, extraction equilibria and solvent sublation for determination of ultra trace Bi(III) and Ti(IV) in water samples by ion-pairs of metal-2-naphthoate complexes and tetrabutylammonium ion, *Bull. Korean Chem. Soc.*, 23 (2002) 1381.
20. H. Izanloo, S. Nasser, Cadmium removal from aqueous solutions by ground pine cone, *Iranian J. Eng. Health Sci. Eng.*, 2 (2005) 33-42.
21. G.M. Payne, A surveyor's perspective: water quality for hemodialysis, advancing safety in medical technology, <http://www.aami.org/publications/hh/Water.quality.Payne.pdf>, accessed in December., 2014.
22. H. Tavallali, A. M. Attaran, Selective determination cloud point extraction trace amounts of silver in water samples by flame atomic absorption spectrometry, *International J. Chem. Tech.*, 2 (2010) 1724-1730.
23. D.L.G. Borges, M.A.M.S. Veiga, V.L.A. Frescura, B. Welz, A.J. Cur-tius, Cloud-point extraction for the determination of Cd, Pb and Pd in blood by electrothermal atomic absorption spectrometry, using Ir or Ru as permanent modifiers, *J. Anal. At. Spectrom.*, 18 (2003) 501.
24. K. Niknam, D. Saberi, M. Mohagheghnejad, Silica bonded S-sulfonic acid: a recyclable catalyst for the synthesis of quinoxalines at room temperature, *Molecules*, 14 (2009) 1915-1926.
25. S. Hssani, A. Moghimi, A. Shahvelaiati, Allogeneic and xenogeneic bone matrix gelatin (bmg) effects on bone defect healing in rats, *Ind. J. Fundament. and Appl. Life Sci.*, 5 (2015) 285-298.
26. M. Ghaedi, M.R. Fathi, A. Shokrollahi, F. Shajarat, Highly selective and sensitive preconcentration of mercury ion and determination by cold vapor atomic absorption spectroscopy, *Anal. Lett.*, 39 (2006) 1171-1180.
27. M. Ghaedi, A. Daneshfar, A. Shokrollahi, H. Ghaedi, A.F. Pili, Highly selective and sensitive spectrophotometric determination of trace amounts of silver ion in surfactant media using 2-mercaptobenzoxazole, *Ann. Chim.*, 97 (2007) 971-979.
28. A. Shokrollahi, M. Ghaedi, R. Shabani, M. Montazerzohori, F. Chehreh, M. Soylyak, S. Alipour, A preconcentration procedure for copper, nickel and chromium ions in some food and environmental samples on modified Diaion SP-850, *Food Chem. Toxicol.*, 48 (2010) 482-490.
29. N. Pourpeza, P. Parham, P. Mirzavand, Flotation-spectrophotometric method for separation and determination of trace amounts of copper, *J. Chem. Soc. Pak.*, 34 (2012) 1352-1355.



30. K. Shawket, J. Jihan, R. Muslim, Cloud point extraction methodology for separation and microamounts determination of lead(II) and cadmium(II) ions, *Iraq. Nat. J. Chem.*, 47 (2012) 401-412.
31. J. Lurie, *Handbook of Analytical Chemistry*, English translated by: N. Bobrov, Moscow, 1978.
32. M. Bahram, S. Khezri, Cloud point extraction, preconcentration and spectrophotometric determination of nickel in water samples using dimethylglyoxime, *Curr. Chem. Lett.*, 2 (2013) 49-56.
33. M. Soleimani, B. Rafiei, Z.H. Siahpoosh, Ghezeljeh montmorillonite nanoclay as a natural adsorbent for solid phase extraction of copper ions from food samples, *J. Anal. Chem.*, 7 (2015) 794-803.
34. I. Svraka, M. Memic, J. Sulejmanovic, T. Muhic-Sarac, Preconcentration of metal ions using silica gel 60 F254, *Bulletin of the chemists and technologists of Bosnia and Herzegovina*, 42 (2014) 11-16.
35. C.A. Kozlowski, M. Ulewicz, W. Walkowiak, T. Girek, the effect of tautomeric rearrangement on the separation of Zn(II) and Cd(II) in ion flotation process with 4-thiazolidinone derivatives, *Minerals Eng.*, 15 (2002) 677-682.
36. E. Metcahf, *Wastewater engineering, treatment and reuse*. McGraw-Hill, (2003) 509-524.
37. F.M. Doyle, Ion flotation-its potential for hydrometallurgical operations. *Int. J. Miner. Process.*, 72 (2004) 387-399.
38. F. Shemirani, B.T.S. Akhavi, Preconcentration and determination of trace cadmium using 1-(2-pyridylazo)-2-naphthol (PAN) immobilized on surfactant-coated alumina, *Anal. Lett.*, 34 (2001) 2179-2188.
39. K. Ghesmat Konande, S. Bagheri, E. Pakdaman, E. Niknam, Ion-flotation Separation of Cd (II) and Ag (I) Traces Using a New Ligand  $\alpha$ -N-Naphtyl-4-Methyl Benzamide (NMBA), before Their Flame Atomic Absorption Spectrometric determination of these ions in radiology wastewater, amalgam, natural water and blood samples, *I. J. Pharm. Res. Alli. Sci.*, 5 (2016) 335-342.
40. H. Karimi, M. Ghaedi, A. Shokrollahi, H.R. Rajabi, M. Soylak, B. Karami, Development of a selective and sensitive flotation method for determination of trace amounts of cobalt, nickel, copper and iron in environmental samples, *J. Hazard. Mater.*, 151 (2008) 26-32.
41. J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*; Ellis Horwood: Chichester, England, 1984.
42. H.A. Panahi, M. Karimi, E. Moniri, H.R. Soudi, development of a sensitive spectrophotometric method for determination of copper, *Afr. J. Pur. Appl. Chem.*, 2 (2008) 96-99.
43. N. Pourreza, H. Parham, P.J. Mirzavand, Flotation spectrophotometric determination of trace amounts of thorium, *Chin. Chem. Soc.*, 54 (2009) 785-788.
44. M.S. Hosseini, H. Hashemi-Moghaddam, G. Kardan-Moghaddam, Separation and preconcentration of Ag(I) in aqueous samples by flotation as an ion associate using iodide and ferroin followed the determination by flame atomic absorption spectrometry *Annali. Di. Chimica.*, 97 (2007) 17-23.