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Ion-flotation Separation of Cd(II) and Ag(I) Traces Using a New Ligand α - 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

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ABSTRACT

A simple, rapid and inexpensive method for separation and pre-concentration of some traces of hazardous elements is presented prior to their flame atomic absorption spectrometric determinations. At pH 9.0±0.1; cadmium(II) and silver(I) were separated simultaneously with α - N– Naphtyl –4 – Methyl Benzamide (NMBA) as a new complexing agent and floated after adding sodium dodecyl sulfate (SDS) as a foaming reagent. The floated layer was then eluted by concentrated nitric acid in methanol and introduced to the flame atomic absorption spectrometer (FAAS). These ions can be eluted quantitatively with 0.5 ml 1M HNO_3 *in methanol. The linear range of the determination is between 0.01-2.2* $\mu g\ mL^{-1}$ *for* Cd^{2+} *and, 0.02-1.9* $\mu g\ mL^{-1}$ *for* Ag^{+} *with a detection limits for ,* Cd^{2+} *and* Ag^{+} *were 1.3 ng* mL^{-1} *and 1.4 ng* mL^{-1}*, respectively. The method has been successfully applied for determination of trace amounts of ions in radiology wastewater, amalgam, natural water and blood samples.*

Keywords: Trace, Ion flotation, ligand α - N– Naphtyl –4 – Methyl Benzamide (NMBA), sodium dodecylsulfate (SDS), Flame atomic absorption spectrometry (FAAS).

INTRODUCTION

The determination of trace metals in the environmental samples including natural waters have been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated [1-3]. The importance of heavy metals and their complex roles in biological systems come from their diverse functions and low level of existence. For instance, some of the trace heavy metals are essential to life while others are toxic even at very low concentrations. However, some of these heavy metals are of particular concern because of their toxicities to humans[4-7], These problems can be overcome by replacement of filtration or centrifugation by flotation. The major advantages of the flotation pre-concentration method are the rapidity in addition to excellent recoveries of investigated trace elements. The equipments necessary for flotation pre-concentration are simple and inexpensive. 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. one of the most important advantages of the flotation method is the ability to analyze a large volume of sample solution and to obtain a greater pre-concentration factor. on the other hand, because the physical and chemical properties of aragonite aqueous solution are similar to those of the natural waters with higher water hardness, a method of flotation is applied as the second way to eliminate the calcium matrix effects [8-11]. Flotation has been used for the recovery of valuable substances from ores and minerals in the mining industry since this century began [12,13]. Step by step, this technique has found applications in different fields of chemical engineering as well as analytical chemistry[14]. Ion flotation, as a flotation subgroup, is a pre-concentration technique known since the early 1960s[15]. It is a simple and inexpensive method for effective removal of ionic species from dilute aqueous solution[16,17]. The major advantages of this method are the rapidity and high recoveries of the trace elements investigated[18]. Several methods have been developed for the flotation of cadmium and silver ions as trace elements[19-21].

The purpose of this work is pre-concentration by flotation of Cd^{2+} and Ag^{+} using NMBA (Figure 1)[22]. The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

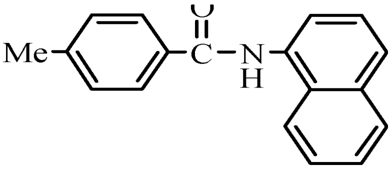

Figure 1: ligand α - N– Naphtyl –4 – Methyl Benzamide (NMBA)

MATERIALS AND METHODS

2.1. Instruments

All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the equipment were established according to the manufacturer's recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements.

2.2. Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of cadmium, silver, mercury, cobalt, iron, nickel, copper, Lead, magnesium, calcium, strontium, barium, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. The ligand α - N– Naphtyl –4 – Methyl Benzamide (NMBA) was synthesized according to literature[22].

2.3. Spectrophotometric titrations

Standard stock solutions of NMBA (10^{-3} M) and the metal ions (3.0×10^{-3} M) were prepared by dissolving appropriate and exactly weighed (accuracy of ± 0.0001 g) amounts of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks, and diluting to the mark with MeOH. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of 2.6 mL of NMBA 2.3×10^{-4} M solution was carried out by the addition of micro-liter amounts of a concentrated standard solution of the metal ion ($1.0 - 2.5 \times 10^{-3}$ M) using a pre-calibrated micro-syringe, at 25.0 °C, with the spectrum subsequently recorded.

2.4. Flotation-separation procedure

A separation funnel with sidelong tube was used for flotation-separation. The separation funnels a sample solution containing 0.2 µg mL^{-1} of each ion, 0.5 mL 1.0 M of HNO_3 solution. 0.25 mL of 0.7% (w/w) solution of SDS and 0.35mL of 10^{-3} M of NMBA were added, the pH of medium was carefully adjusted to 9.0±0.1 with nitric acid or sodium hydroxide solution . The mixture was diluted to 10 mL and after stirring for 20 min. then an air stream (10 mL min^{-1}) was kept flowing for 2-4 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 ml1.0 M HNO_3 in methanol and then the metal ions content was readily evaluated by FAAS.

2.5. Application to Real Samples

Real samples including blood samples were treated as described previously [23]. Then the Test Procedure described above was applied. For the application of the present procedure to amalgam alloy, an accurately weighed 0.4 g portion of each amalgam alloy sample was digested as described previously [24,25]. and dissolved in the smallest volume of water, and the solution was transferred to a 100 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 silver content as follows. To 20 mL sample were added about

10 mL 3M nitric acid and 10 mL water. The solution was boiled until its volume was reduced to20 mL. The resulting solution was neutralized with NaOH solution to the desired pH value and filtered. The filtrate and washings were diluted to 50 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 Ag^+ and Cd^{2+} ions 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 NMBA concentrations, heating time and temperature, centrifuge time and rate, 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 [26], before using NMBA for the flotation of the metal ions.

3.1. Investigation of ligand complexation with metal ions

The complexation studies between the ligand and Cd(II) and Ag(I) ions were carried out to determine the stoichiometry of the metals - ligand reactions as well as the formation constants and the molar absorptivities of these complexes. The stoichiometry between the ligand and each of the metal ions were determined from the absorbance-mole ratio data. The plots at 469 nm (Figure 2), clearly show a 1:1 (ligand to metal) stoichiometry for all themetal complexes. The formation constants, K_f, and the molar absorptivities, ε_{ML}, of the resulting complexes were then evaluated from the absorbance-mole ratio data and with the aid of a nonlinear curve fitting of the theoretical absorbance, A_{Theo}, to the experimental absorbance, A_{Exp}, using Microsoft Excel Solver program. When known concentrations of metal, C_M, is mixed with a constant concentration of ligand and ML complexes are formed, the following equations can be written;

$L + M \leftrightarrow ML \qquad Kf = [ML] / [L] [M]$

$[L] = C_L - C_M + x \qquad [M] = x \ [ML] = C_M - x$

$K_f \ x^2 + (K_f C_L - K_f C_M + 1) x - C_M = 0$

$A_{Theo} = A_L + A_{ML} = (A_0 / C_L)[L]$
$+ \varepsilon_{ML} K_f C_M [L] / (1+K_f [L])$ (2)

where A_0 is the initial absorbance of the ligand with concentration of C_L before any metal ions addition. Also, x is a reversed amount of ligand or metal reproduced from decomposition of ML at equilibrium which is equal to [M] value under $C_M \geq C_L$ condition. The procedure actually consists of two mutual steps. First, by initial guessing for K_f and solving Equation (1), x value is obtained which yields [L] parameter from $[L] = C_L - C_M + x$ then A_{Theo} is calculated by the substitution of [L] in Equation (2) (C_L, C_M and A_0 are known parameters). In the second step, for fitting the curve of A_{Theo} to that of A_{Exp}, minimization of SSR, sum of squared of residual, is performed by the Excel Solver program and two adjustable parameters K_f and ε_{ML} are found. The results, which are summarized in (Table 1), show the values of formation constants for the considered metal complexes.

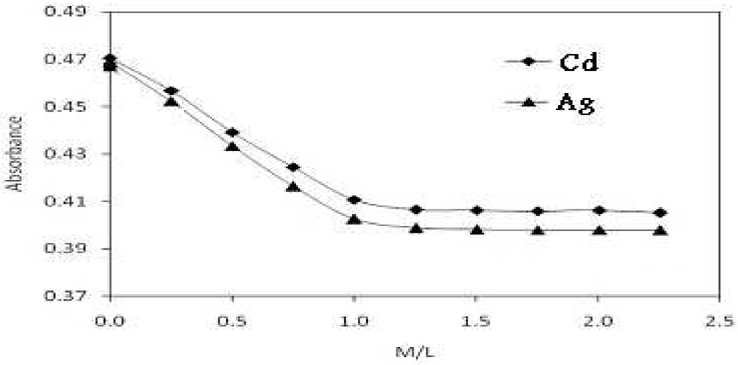

Figure 2. Absorbance-mole ratio plot for Cd- NMBA and Ag- NMBA complexes at [M] = 469 nm, [NMBA] = 1.5 × 10-4mol/L in Methanol

Table 1. Formation constants and molar absorptivities of the metal complexes

Type of complex	K_f	ε_{ML}	SSR[a]
Cd— NMBA	1.02×10^6	2.71×10^3	1.22×10^{-5}
Ag— NMBA	1.17×10^6	2.65×10^3	1.22×10^{-6}

[a] SSR = $\sum$ $(A_{Exp} - A_{Theo})2$

3.2. 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. Extraction yield depends on the pH at which complex formation is carried out. Thus, a set of similar experiments in the pH range 2.0-12.0 was conducted according to the described procedure described in the experimental section with respective results illustrated in Figure 3. The maximum sensitivity by flotation was obtained at pH 9.0±0.1, In more acidic solutions, deterioration of the signal occurs due to protonation of NMBA, while at pH > 9.0±0.1, the signal decreases and recovery is reduced due to precipitation of Cd^{2+} and Ag^+ ions in the form of hydroxides or ternary complexes. Consequently, pH = 9.0±0.1, was selected for the subsequent studies.

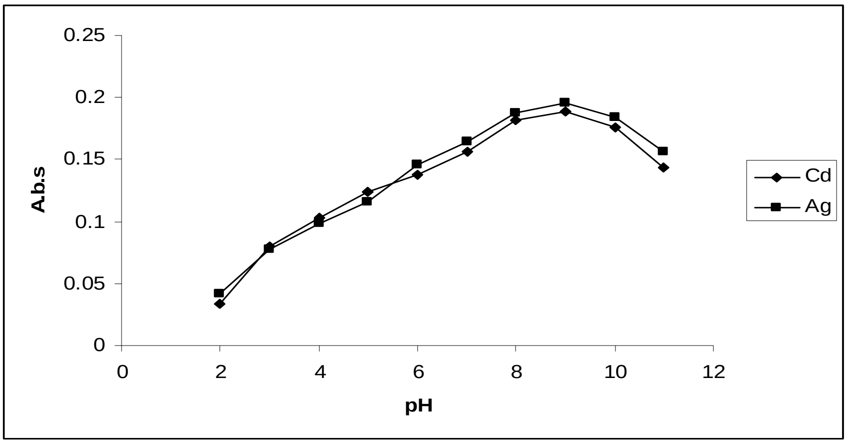

Figure 3: Effect of pH on ions recoveries

3.3. Influence of NMBA 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 1.0×10^{-4} to 3.5×10^{-3} mol/L of NMBA. At pH = 9.0±0.1, 25 mL of a sample solution containing 3.5×10^{-4} mol/L of each of the metal ions and 4 mL the perfect flotation separation of the metal ions was achieved at NMBA concentration greater than 3.5×10^{-4} mol/L Figure4. Thus, the solution of NMBA with concentration of 3.5×10^{-4} mol/L was used for subsequent experiments. Since the separation efficiency remained constant in the presence of excess amounts of NMBA, this ligand could easily be used for investigation of the samples containing unknown amounts of the analytes.

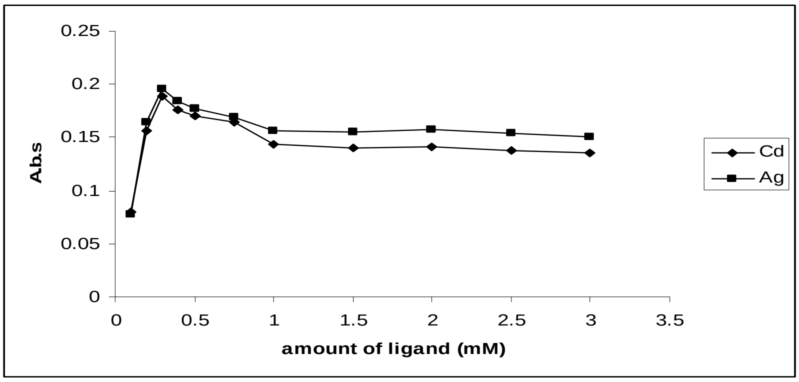

Figure 4: Effect of NMBA on ions recoveries

3.4. 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 Table2. The flotation by use of TX-100 and TX-114 was also ineffective. The anionic surfactants were more effective. The ions flotation recoveries obtained by SDS within the optimal pH range 9.0±0.1, were greater than 97.8 – 98.2%. The anionic surfactant SDS was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost.

Table2. Effect of type of surfactant on sensitivity for 0.2 μg mL^{-1} of interest ion, pH 9.0±0.1, NMBA (3.5 × 10^{-4}mol/L) and 0.5 % (w/v) of each surfactant

Surfactant t	Cd %	Ag%
Triton X-114	48.7	53.7
SDS	97.8	98.3
Triton X-100	56.7	49.8
No surfactant	25.9	30.4

The flotation efficiency was evaluated using SDS concentrations ranging from 0.05% to 1.0% (w/v). The highest cadmium and silver ions recovery was obtained with 0.5% (w/v) SDS. By decreasing the surfactant concentration to 0.5% (w/v) the recovery was reduced. The cadmium and silver ions recovery also decreased for a higher SDS concentration (0.5% 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 [28,29]. At lower SDS concentrations (below 0.5% 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 [29-31]. Since, 0.5% (w/v) of SDS showed the highest cadmium and silver ions recovery; a surfactant concentration of 0.5% (w/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration.

3.5. 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 KNO_3 salt as an electrolyte in the range 0.01-0.5 mol L^{-1} on the process was investigated. It is observed that increasing concentration of salt to 0.1 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.

3.6. Calibration, precision and detection limits

Calibration graphs were obtained by pre-concentration of 25 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 FAAS. A linear relationship between the measured absorbance and concentration of Ag^+ or Cd^{2+} ions in the Linear Range 0.01-1.3μg mL^{-1} and 0.02-1.7μg mL^{-1} was obtained. Table3. 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 Ag^+ and Cd^{2+} ions were 1.1 (ng mL^{-1}) and 0.9 (ng mL^{-1}), respectively.

3.7. Flotation mechanism

There are in fact two main types of interactions involved in the process of flotation, namely physical and electrostatic interactions [32,33]. 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 solid species and 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.

3.8. Characteristics of the method

Table 3: Specification of presented method at optimum conditions for each element

Parameters	Cd	Ag
Linear Range (μg mL^{-1})	0.01-2.2	0.02-1.9
Detection Limit (ng mL^{-1})	1.3	1.4
RSD %	1.3	1.6
Recovery%	98.7	98.2

3.9. Interference study

With a view to obtaining high selectivity by the FAAS method, the interferences were studied. These interferences constitute special ions which are related to the pre-concentration step, *i.e.* those that may react with NMBA and decrease the pre-concentration and extraction efficiency (Table 4). The study of possible interferences was conducted for Li^+ , K^+ , Na^+, Ni^{2+}, Pb^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+} , $NO_3{}^-$, $SO_4{}^{2-}$, $ClO_4{}^-$, Cl^- and Cd^{2+} or Ag^+ ions under the experimental conditions (at a fixed concentration of 66.7 or 133.3 µg L^{-1} of Ag^+ or Cd^{2+}, respectively). There was no significant interference at a 1:1000 ratio of Ag^+ or Cd^{2+} with Li^+, K^+, Na^+, Ni^{2+}, Pb^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cr^{3+} , NO_3^-, ClO_4^-, Cl^- and SO_4^{2-} ions, and also for the same condition at a ratio of 1:500 Ag^+ or Cd^{2+} with Cu^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+} , and Cd^{2+} or Ag^+ ions.

Table 4: Effects of the matrix ions on the recoveries of the examined metal ions (N=5)

Analyte	Ions	Interference/ analyte ratio(µg L^{-1})	Recovery (%)
Ag^+	Li^+, K^+, Na^+, NO_3^-, Cl^-	1000	101.2
	Ca^{2+}, Mg^{2+}, Ba^{2+}	1000	100.3
	Cu^{2+}, Mn^{2+}, Cd^{2+}	500	99.1
	Fe^{3+}, Al^{3+}	500	99.3
	Cr^{3+}	1000	98.9
	Ni^{2+}, Pb^{2+},CO^{2+}	1000	100.2
	SO_4^{2-}, CLO_4^-	1000	99.8
Cd^{2+}	Li^+, K^+, Na^+, NO_3^-, Cl^-	1000	100.1
	Ca^{2+}, Mg^{2+}, Ba^{2+}	1000	101.0
	Cu^{2+}, Mn^{2+}, Ag^+	500	99.8
	Fe^{3+}, Al^{3+}	500	99.4
	Cr^{3+}	1000	100.1
	Ni^{2+}, Pb^{2+},CO^{2+}	1000	100.4
	SO_4^{2-}, CLO_4^-	1000	99.7

3.10. Real samples – evaluation of method

The proposed method was applied for the determination of Ag^+ and Cd^{2+} ions by the standard addition technique in radiology wastewater, amalgam, natural water and blood samples. including well radiology wastewater and amalgam samples (Table 5). The results of in natural water and blood samples. as mentioned in the Experimental section are summarized in Table 6. Notably, the determination of Ag^+ and Cd^{2+} in radiology wastewater, amalgam, natural water and blood samples. is remarkably accurate by the proposed method. The results of the determination of Ag^+ and Cd^{2+} in the in radiology wastewater, amalgam, natural water and blood samples. as mentioned in the experimental section are listed in Table 6.

Table 5: Recovery of trace elements from radiology wastewater and amalgam samples after application of presented flotation procedure(N=3)

Ion	Added, µg L^{-1}	Found, µg L^{-1}	RSD %	Recovery %
Radiology wastewater				
Cd	0	0.17	1.6	---
	0.5	0.66	1.2	98.4
Ag	0	1.6	1.4	---
	0.5	2.1	1.0	101.1
Amalgam				
Cd	0	0.06	1.4	---
	0.5	0.51	1.1	103.6
Ag	0	0.4	1.2	---
	0.5	0.9	0.9	102.1

Table 6: Recovery of trace elements from natural water and blood samples after application of presented flotation procedure(N=3)

Ion	Added, µg L^{-1}	Found, µg L^{-1}	RSD %	Recovery %
Blood				
Cd	0	0.7	1.5	---
	10	1.8	1.2	103.0
Ag	0	0.02	1.2	---
	10	013	0.9	100.6
Natural water				
Cd	0	0.5	1.2	---
	10	1.4	1.1	101.2
Ag	0	0.04	1.5	---
	10	0.07	1.2	99.0

CONCLUSION

In the presence of NMBA as a new ligand and with the aid of flotation method, a successful samples. The mechanism of complaxation between the metal ions, the ligand and SDS is suggested as the following: once a metal ion bonds with the ligand and a positively charged ion complex is formed, the SDS (with negative charge on the sulfate group) interacts with it, and a self-floatable [M - NMBA - SDS] species is formed. The species, then, attaches to the air bubbles from the hydrophobic part of the surfactant and floats on the surface. The relatively high enrichment factors and the low detection limits, reported in section[34 , 35], were obtained throughout the study along with a reasonable accuracy and precision. The efficiency of the ligand as an impressive sorbent agent for Cd(II) and Ag(I) traces was indicated by evaluating large formation constants, K_f, and molar absorptivities, ML, of the complexes. Some individual features of the proposed method such as simplicity, convenience; ecological safety and low cost were obviously experienced during the investigation. Also, a comparison between the proposed method and two common types of pre-concentration techniques, cloud point extraction and solid phase extraction, from recent papers is made in (Table 7). The capability of the method was also demonstrated by applying to the radiology wastewater, amalgam, natural water and blood samples. The data obtained from the investigations on the radiology wastewater, amalgam, natural water and blood revealed the relatively higher levels of the heavy metals, especially cadmium and silver ions, in these samples in comparison with those of normal real reported by different sources [36], which can be attributed to the existence of these elements in radiology wastewater, amalgam, natural water and blood products.

Table 7. Comparative data from recent papers on preconcentration studies

Analytes	Methodand apparatus	EF	DL (μg/L)	R.S.D. (%)	Ref.
Cd(II), Pb(II), Ag(I)	CPE/FAAS	48.0,39.0,42.0	1.4, 2.8, 1.4	<3.6	[37]
Ag(I)	CPE/FAAS	39.0	1.9	<1.7	[38]
Cd(II), Zn(II)	CPE/FAAS	23.9,25.6	3.0, 2.0	<3.3	[39]
Cd(II), Co(II), Pb(II)	SPE/FAAS	50.0	1.2-3.1	1.0-3.2	[41]
Cd(II)	SPE/FAAS	75.0	0.6	<3.7	[41]
Cd(II), Zn(II), Ni(II)	SPE/FAAS	80.0	2.1–2.3	1.23–1.31	[42]
Cd(II), Ag(I)	Ion Flotation/FAAS	38.5 , 39.2	1. 3 , 1.4	<2.0	Present work

[a]*EF: enrichment factor, DL: detection limit, R.S.D.: relative standard deviation; SPE: solid phase extraction, CPE: cloud point extraction, CE: capillary electrophoresis, N. R.: not reported.*

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REFERENCES

[1] Uluozlu, O. D, Kinalioglu, K, Tuzen, M, Soylak, M (**2007**), *Biomed. Environ. Sci.* 20, 203.
[2] Xu, H, Zeng, L P, Xing, S J, Jin, L T (**2008**) *Chin. J. Chem.*, *26*, 847.
[3] Tuzen, M, Sesli, E, Soylak M (**2007**) , *Food Control* 18, 806.
[4] Nardi, E. P, Evangelhista, F. S, Tormen, L, Saint'Pierre, T. D, Curtius, A. J, Souza, S. S. J, Barbosa, F(**2009**) *Food Chem*, *112*, 727.
[5] Sesli, E, Tüzen, M, Soylak, M(**2008**) *J. Hazard. Mater*, *160*, 462.
[6] Kazi, T. G,Jalbani, N, Jamali, M. K, Arain, M. B,Afridi, H. I, Kandhro, A, Pirzado, Z(**2008**) *Renal Failure*, *30*, 737.
[7] Arce, S, Cerutti, S, Gomez, M. R, Martinez, L. D(**2008**) *J. AOAC In.*, *91*, 853.
[8] Stafilov, T, Lazaru A (**1996**), *Geologica Macedonica* 10, 83.
[9] Lazaru, A, Stafilov T (**1997**) , *Anal. Lab*. 6, 101.
[10] Stafilov, T, Zendelovska D (**2000**) , *Acta Chim. Slov.* 47, 381.
[11] Mizuike, A Flotation, Chapter 10, (**1983**) Enrichment Techniques for Inorganic Trace Analysis, Springer-Verlag, Berlin, pp. 94–99.
[12] Lemlich, R. *Adsorptive Bubble Separation Techniques*(**1972**) Academic Press: New York, p 3351.
[13] Grieves, R. B,(**1975**) *Chem. Eng. J*, *9*, 93.
[14] Mizuike, A, Fresenius (**1986**) *J*, *Anal. Chem*, *324*, 672.
[15] Cabezon, L. M.; Caballero,M.; Cela, R.; Perez- Bustamante, J. A(**1984**) *Talanta*, *31*, 597.
[16] Pavlovska, G,Stafilov, T, Cundeva, K(**2001**) *J. Anal. Chem*, *369*, 670.
[17] Stafilov, T, Pavlovska, G, Cundeva, K(**2000**) *Turk. J. Chem*, *24*, 303.
[18] Caballero, M, Cela R, Perez-Bustamante J A, (**1990**) Analytical Applications of Some Flotation Techniques – A Review, *Talanta* 37, 275.

[19] Cundeva K, Stafilov T, Pavlovska G (**2000**) , *Microchem. J.* 65 , 165.
[20] Paneva V Z, Cundeva K, Stafilov T (**2005**) , *Spectrochimica Acta* B 60, 403.
[21] Zendelovska D, Pavlovska G, Cundeva K, Stafilov T (**2001**) , *Talanta* 54,139.
[22] Niknam, K, Zolfigol ,M A, Sadabadi, T (**2007**), *J. Iran. Chem. Soc* 4, 199.
[23] Ghaedi, M, Ahmadi, F, & Soylak, M. (**2007**) *J. Hazard. Mater.* 147, 226.
[24] Ghaedi, M, Fathi, M.R, Shokrollahi, A, & Shajarat, F. (**2006**) *Anal. Lett.* 39, 1171.
[25] Ghaedi, M, Daneshfar, A,Shokrollahi, A,Ghaedi, H, & Pili, A.F. (**2007**) *Ann. Chim.* 97, 971.
[26] Shokrolahi, A, Ghaedi, M, Shabani, R, Montazerozohori, M, Chehreh, F, Soylak, M.; Alipour, S(**2010**) *Food Chem. Toxicol*, *48*, 482.
[27] Ghaedi, M, Shokrollahi, A, Niknam, K, Niknam, E, Derki, S, Soylak, M. (**2009**), at Subtrace Levels in Environmental Samples *J. AOAC Int. 92* , 35 - 42.
[28] Martell A E, Motekaitis R J(**1992**) Determination and Use of Stability Constants, VCH Publishers, New York
[29] Pinto C G, Pavo´n J L P, Cordero B M (**1996**) *J. Anal. At. Spectrom*. 11,37.
[30] Ahmadi, F, Niknam, E, iknam, K. (**2011**), *Arabian Journal for Science and Engineering*, 36, 47.
[31] Silva. EL, Roldan. PD, (**2009**), *Journal of Hazardous Materials*, 161, 142.
[32] Tavallali, H, Attaran**,** A. M, (**2010**), *International Journal of ChemTech*, 2 (3),1724.
[33] Hosseini,MS, Hashemi-Moghaddam, H, Kardan-Moghaddam,G.(**2007**), *Annali Di Chimica* 97 (1-2),17.
[34] Tüzen, M (2003) *Food Chem, 80*, 119.
[35] Afridi, H. I, Kazi, T. G, Kazi, N, Jamali, M.K, Kazi, G. H, Arain, M. B, Shah, A. Q, Jalbani, N (**2008**) *Diabetes Res. Clin. Pr, 80*, 280.
[36] Wilhelm, M, Lombeck, I, Ohnesorge, F. K (**1994**) *Sci. Total Environ*, *141*, 275.
[37] Ghaedi, M, Shokrollahi, A, Niknam, K, Niknam, E, Najibi, A, Soylak (**2009**) M. *J. Hazard. Mater*, *168*, 1022.
[38] Ahmadi, F, Niknam, E , Niknam, K. (**2011**), *E-Journal of Chemistry*. 8(1): 435- 442.
[39] Shokrollahi, A, Haghighi, H. E, Niknam, E, Niknam, K (**2013**) *Quím. Nova São Paul* , 36: 3, 273 – 283.
[40] Marahel, F, Ghaedi, M, Shokrollahi, A, Montazerozohori, M, Davoodi, S (**2009**) *Chemosphere*, *74*, 583.
[41] Liang, P, Peng, L (**2010**), *Talanta* 81, 673.
[42] Ghaedi, M, Niknam, K, Zamani, S, Abasi Larki , H, Mostafa Roosta, M, Soylak, M (**2013**), *Materials Science and Engineering* , 33 , 3180.