

Micelle mediated methodology for the determination of heavy metals in real samples by flame atomic absorption spectrometry

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ABSTRACT

A simple and sensitive method is described for the pre-concentration by cloud point extraction followed by atomic absorption spectrometric determination of nickel, lead, zinc and copper ions in real samples. At a solution pH of 7.0, 2-amino-5-mercapto-1, 3, 4-thiadiazole (AMTD) and Triton X-114 were used as hydrophobic ligand and non-ionic surfactant. The adopted concentrations for AMTD, Triton X-114 and HNO_3 , bath temperature, centrifuge rate and time were optimized. Detection limits (3SDb/m) of 1.4, 1.6, 1.7 and 1.5 $ng\ mL^{-1}$ for Ni^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} along with enrichment factors of 29 for these ions were achieved. The presented procedure was applied to the determination of analytes in cow liver, natural and industrial waste water and blood samples with successful results (recoveries greater than 97%, R.S.D., lower than 1.8 % for $N=3$).

Keywords: 2-Amino-5-mercapto-1, 3, 4-thiadiazole (AMTD), nickel, lead, zinc, copper, cloud point extraction; Flame Atomic Absorption Spectrometry (FAAS).

INTRODUCTION

Several analytical techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace metals with sufficient sensitivity for most applications. However, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrix effects. Pre-concentration and separation can solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS) (Chen & Teo, 2001, Ahmadi *et al.*, 2008). There are many

methods of pre-concentration and separation, such as ion-exchange techniques (Prakash *et al.*, 1989, Ebdon *et al.*, 1991.), co-precipitation (Vircaus *et al.*, 1994, Chen. *et al.*, 2005, Shemirani. *et al.*, 2006) and other sorbents (Mohammad *et al.*, 1992, Sutton *et al.*, 1996, Zougagh *et al.*, 2005, Ahmadi *et al.*, 2008).

Separation and pre-concentration based on cloud point extraction (CPE) is becoming an important and practical application in the use of surfactants in analytical chemistry (Sanz-Medel *et al.*, 1999, Stalikas, 2002). The principle, advantages and applications of CPE have been well-established and identified in recent years. The use of pre-concentration steps based on CPE offers a conventional alternative to more traditional extraction systems and permits the design of extraction schemes that are simple, cheap, of high efficiency and of lower toxicity than extractions that use organic solvents. To date, CPE has been used for the extraction and pre-concentration of metal ions after the formation of sparingly water-soluble complexes, and then the complex in the surfactant-rich phase is determined by different spectrometric methods (Gallindo *et al.*, 2003, Wuilloud *et al.*, 2002).

In the present work, we report on the results obtained from applying the CPE for the extraction of nickel, lead, zinc and copper from real samples and their determination by atomic absorption spectrometric.

EXPERIMENTAL

Apparatus

A Shimadzu AA-680 atomic absorption/ flame emission spectrometer equipped with deuterium background correction was used with nickel, lead, zinc and copper hollow-cathode lamps as radiation sources. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in 0.5 mol L^{-1} HNO_3 in methanol. For discrete volume sampling, a volume of 500 μL of the final solution was introduced into the nebulae of the spectrometer by a manual sample injection that was connected to the nebulae by the sample aspiration tubing. The conditions for FAAS determination of metal ions are presented in Table 1. Absorbance signals as peak height were measured. A Metrohm 691 pH /Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. A MP4 centrifuge (International Equipment Company, USA) was used to accelerate the phase separation.

Table 1: Hollow cathode lamp conditions and flame conditions for FAAS in determination of metal ions

Element	Slit(nm)	Wavelength(mA)	Flow rate of flame gases (Lmin-1)	
			Air	Acetylene
<i>Cu</i>	0.5	324	8.0	1.8
<i>Ni</i>	0.15	232	8.0	1.7
<i>Pb</i>	0.3	217	8.0	1.8
<i>Zn</i>	0.5	213.9	8.0	2.0

Reagents and solutions

All chemicals used in this work were of analytical reagent grade and were used without further purification. Deionized water was used for all dilutions. A 0.5 % (w/w) Triton X-114 from Merck Company was prepared by dissolving 0.5 gr of Triton X-114 in distilled water in 100 mL volumetric flask with stirring. Stock standard solutions of nickel, lead, zinc and copper at concentration of $1000\mu\text{g mL}^{-1}$ were obtained from Sectors. Working standard solutions were obtained by appropriate dilution in water of the stock standard solutions. A solution of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ AMTD (Merck, Darmstadt, Germany) in water was prepared from the commercially available product. Nitric acid (Merck) and methanol (Merck) for discrete volume sampling were used. A stock standard buffer solution, 0.2 mol L^{-1} , was prepared by dissolving appropriate amounts of $\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in water.

Cow liver sample

A 50 g sample of cow Liver was taken and dried for 48 hours in an oven at 120°C to remove the water content and to obtain a constant weight (about 68% water). Dried liver sample was transferred into a glass flask. For the digestion of the sample, a concentrated acid mixture of 3 mL H_2SO_4 , 15 mL HClO_4 , and 15 mL HNO_3 was added and left to stand over night. The solution was kept in an oil bath at 50°C until the foaming stopped. Then the temperature was increased to 150°C and heating was continued until the brown fumes of nitrogen oxides ceased. When a dark brown color in the mixture appeared, the flask was cooled for about two minutes, then 5 mL of nitric acid had to be added. Heating was continued until nitrogen oxide fumes were completely given off. The appearance of a white fume of perchloric acid in a 1 mL solution is an indication of complete digestion (Ghaedi *et al.*, 2005, Ahmadi *et al.*, 2008).

Water samples

An analysis of water samples for determination of metal ions content was performed as follows: 400 mL of sample was poured in a beaker and 8 mL concentrated HNO_3 and 3 mL of H_2O_2 (30%) were added for elimination and decomposition of the organic compound. The samples, while being stirred, were heated to one tenth volume. After adjustment of the samples, pH to the desired value, the CPE were performed according to the general described procedure (Ghaedi *et al.*, 2006, Ahmadi *et al.*, 2008).

Human blood sample

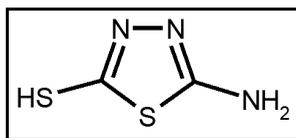
A human blood sample (20 mL) was placed in a 200 mL beaker and was digested in the presence of a mixer oxidizing agent with the addition of 10 mL concentrated HNO_3 (37%) and 2 mL $HClO_4$ (70 %) were added and heated for 1 hour. The contents of the beaker were filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and diluted to the mark with de-ionized water; its pH was adjusted to the desired value. In all, amounts of metal ions were found by the standard addition method (Ghaedi, 2007).

Procedure

For CPE, an aliquot of 15 mL of a solution containing metal ions, 0.1 % Triton X-114, 0.2% (w/v) $NaCl$ and 0.27 mmol L^{-1} of AMTD, was adjusted to pH 7.0 with buffer solution. The mixture was kept for 15 minutes in a thermostatic bath maintained at 40°C . The phase separation is accelerated by centrifuging at 4000 rpm for 15 minutes. The whole system was cooled in an ice-bath for 15 minutes so that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted, The remaining micellar phase was dissolved in $500 \mu\text{L}$ of $0.5 \text{ mol L}^{-1} HNO_3$ in methanol, and then the metal ions content was readily evaluated by FAAS.

Results and discussion

We studied different metal ions with 2-amino-5-mercapto-1, 3, 4 -thiadiazole (AMTD). Due to the existence of a donating atom as well as -S (SH) group and NH group in 2-amino-5-mercapto-1, 3, 4 -thiadiazole (AMTD) it was expected to increase both the stability and selectivity of its complex toward ions. It occurred to us that the presence of some constituents with non-cyclic sulfur-containing ligand in addition to nitrogen and sulfur the π -electrons results in selective interaction with these ions (Ghaedi *et al.*, 2007).



Scheme 1: 2-amino-5-mercapto-1, 3, 4-thiadiazole (AMTD)

Effect of PH

CPE of nickel, lead, zinc and copper was performed in different pH buffer solutions. The separation of metal ions by the CP method involves formation of a complex with a ligand of sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase, to reach the desired pre-concentration. Extraction yield depends on the pH at which complex formation occurs.

The effects of pH on the extraction of metal complexes are given in Fig 1. In the pH range 6.5-7.0, extraction was quantitative. The decrease in recoveries at pH > 7.0 is probably due to the precipitation of metal ions in the form of hydroxide, and at pH < 6.5 may be due to competition from the hydronium ion toward ions for complexation with AMTD or decomposition of complex at pH values smaller than 6.5, which led to the decrease in recoveries. In subsequent experiments a pH of 7.0 was selected.

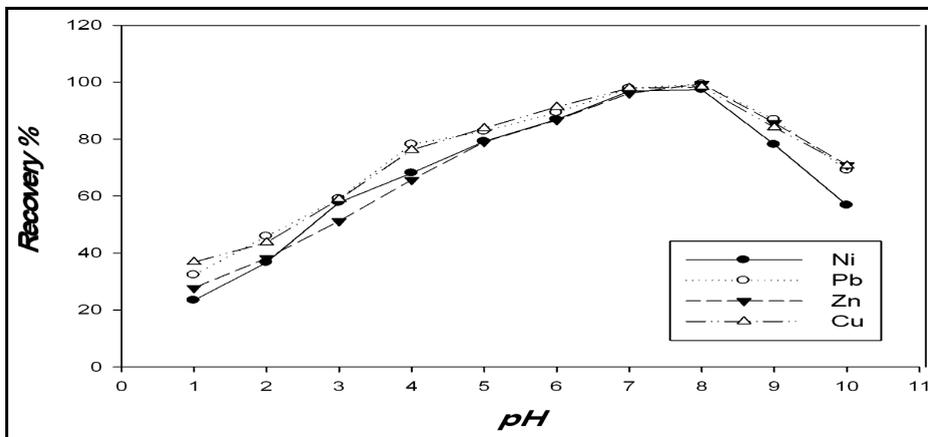


Fig.1 Effect of pH on the extraction recoveries of metal ions.

Effect of ionic strength

Studies on the effects of some additives, such as anionic and non-ionic surfactants and electrolytes *NaCl*, *KNO₃* and *MgCl₂*, on the cloud point

behavior of non-ionic surfactants have been reported (Gu & Galera-comez, 1995, Broos *et al.*, 2005, Din *et al.*, 2008). It was observed that the presence of electrolytes decreases the cloud point (salting-out effect), resulting in a more efficient extraction. The lower cloud point is attributed to electrolytes promoting dehydration of the poly (oxyethylene) chains (Tani *et al.*, 1998, Fang *et al.*, 2000, Teo & Chen, 2001, Din *et al.*, 2008).the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles, increasing inter-attraction between micelles and consequently leading to the precipitation of surfactant molecules. in Fig 2, based on this discussion, *NaCl* was investigated as the electrolyte in the concentration range from 0.01 to 1% (w/v), and the highest metal ions recovery were obtained at 0.2% (w/v) *NaCl* concentration. The signal decreased considerably for increasing *NaCl* concentrations (0.3-1% w/v). This effect might be explained by the additional surface charge when the *NaCl* concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained.because of this, 0.2% (w/v) *NaCl* concentration was used in all further experiments.

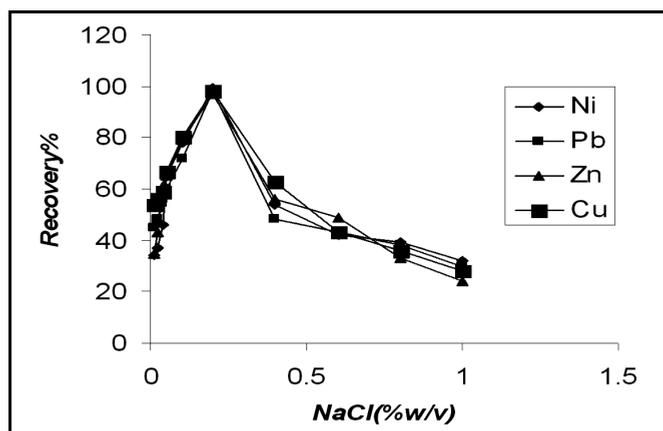


Fig.2 Effect of ionic strength on the extraction recoveries of metal ions.

Effect of AMTD concentration

The effect of the concentration of the chelating agent on the analytical signal was examined and the results are shown in Fig. 3. Major improvement in the responses was obtained as the chelating agent concentration increased up to certain values, which are sufficient for total complexation and the extraction. A concentration of 0.27 mM (2.0 ml from $2.0 \times 10^{-3} \text{ M}$ solution) was chosen as the optimum concentration of the chelating agent for CPE of metal ions.

Concentrations above this value have no significant effect on the performance of the system. The slight difference in the behaviour of AMTD with metal ions is probably due to different chelate formation constants.

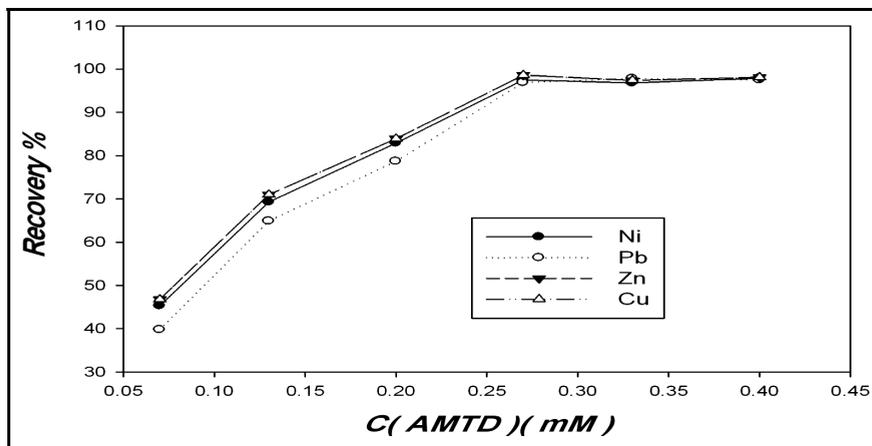


Fig. 3 Effect of AMTD concentration on the extraction recoveries of metal ions.

Effect of Triton X-114 concentration

The pre-concentration efficiency was evaluated using variable Triton X-114 concentrations ranging from 0.03% to 0.22% (w/v). The results are demonstrated in Fig 4. As can be seen, the highest metal ions recovery was obtained with 0.1% (w/v) Triton X-114. By decreasing the surfactant concentration to 0.03% (w/v) the recovery is reduced. The metal ions recovery also decreased for a Triton X-114 concentration greater than 0.1% (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 (Fang *et al.*, 2000, Teo & Chen, 2001, Din *et al.*, 2008). At lower Triton X-114 concentrations (below 0.03% w/v), the pre-concentration efficiency of the complex was very low, probably due to an inability for quantitative entrapment of hydrophobic complex (Boyukbayram & Volkan 2000, Meeravalli *et al.*, 2007).

The optimum surfactant concentrations are same for all analyses. An amount of 0.1% Triton X-114 was chosen in order to achieve the greatest analytical signal and thereby the highest extraction efficiency.

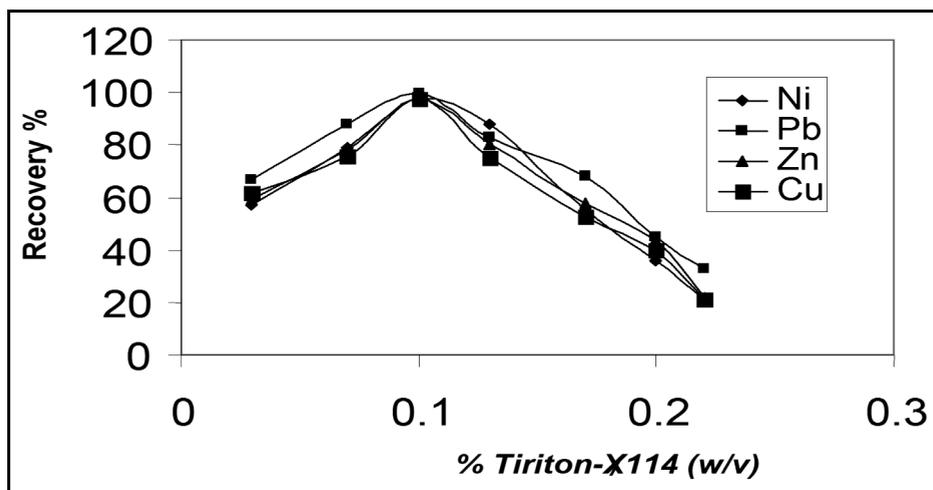


Fig. 4 Effect of Triton X-114 on the extraction recoveries of metal ions.

Effect of methanol

Since the surfactant-rich phase obtained after the cloud point pre-concentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small ($500\mu\text{L}$), methanol containing $0.5\text{ mol L}^{-1}\text{ HNO}_3$ was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume ($500\mu\text{L}$) with respect to the metal ions recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measure the absorbance. Larger volumes of acidified methanol dilution clearly predominated, resulting in a gradual absorbance reduction. A $500\mu\text{L}$ volume of methanol was therefore used throughout the remaining experiments.

Effect of other experimental factors

The incubation time and equilibration temperature above the cloud point were thoroughly optimized. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases. The dependence of extraction efficiency on equilibration temperature and time were studied within a range of $25\text{-}60^\circ\text{C}$ and $10\text{-}50\text{ min}$, respectively. The results showed that an equilibration temperature of 40°C and an equilibration time of

15 minutes are adequate to obtain quantitative extraction of all ions. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5-25 minutes. A centrifugation time of 15 minutes at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative.

Effect of foreign ions

The influences of some alkaline and alkaline-earth ions and transition metal ions on the metal ions recovery of the analyte ion were investigated by the presented CPE procedure. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the pre-concentration and determination of metal ions. metal ions were quantitatively recovered in the presence of large amounts of alkaline and alkaline earth ions and some transition metal ions. The matrix ion contents in the final solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

Table 2: Effects of the foreign ions on the recoveries of the examined metal ions ($N=3$)

Ions	Added As	Tolerance Limit, mg L-1
Cl, K^+, Na^+	$KCl, NaCl$	1000
Mg^{2+}	$MgCl_2$	1000
HCO_3^-	$NaHCO_3$	850
Fe^{2+}, Mn^{2+}	Nitrate salts	750
CO_3^{2-}	Na_2CO_3	750
$Co^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}$	Nitrate salts	550
Ag^+, Hg^{2+}	Nitrate salts	350

Figures of merit

Calibration graphs were obtained by pre-concentrating 15 ml of a sample containing known amounts of all analyses under the experimental conditions. Table 3 features the analytical characteristics of the method. Under the specified experimental conditions the calibration curves for *Ni*, *Pb*, *Zn* and *Cu* were linear from 0.03- 0.5, 0.05-0.5, 0.01-0.3 and 0.02-0.2 $\mu g mL^{-1}$, respectively.

Table 3: Specification of method at optimum conditions for each element ($N=3$)

Parameter	Ni	Pb	Zn	Cu
Linear Range ($\mu\text{g mL}^{-1}$)	0.03-0.5	0.05-0.5	0.01-0.3	0.02-0.2
Linear equation	$A=1.950C_{\text{Ni}}-0.051$	$A=1.893C_{\text{Pb}}-0.0124$	$A=1.974C_{\text{Zn}}-0.003$	$A=1.803C_{\text{Cu}}-0.081$
Detection Limit (ng mL ⁻¹)	1.4	1.6	1.7	1.5
RSD%	1.2	1.3	1.5	1.7
LOQ	4.7	5.3	5.7	5.0
Recovery%	98.4	99.8	98.4	99.2
EF	29	29	29	29

Determination of metal ions in real samples

In order to validate the proposed methodology, the procedure was applied to the determination of metal ions in real samples. For this purpose, 15 ml of each of the samples were pre-concentrated with 0.1% (w/v) Triton X-114 and AMTD concentration of 0.27 mM following the proposed procedure. The procedure was applied to the determination of metal ions in different samples including natural water, waste water, blood and cow liver samples by the standard addition method. Reliability was checked by spiking experiments. The results are shown in Tables 4 and 5.

Table 4: Recovery of trace elements from waste water and river water samples after applicatio of the proposed CPE procedure ($N=3$)

Element	Waste Water				River Water			
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	RSD%	Recovery %	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	RSD%	Recovery %
Ni	0	56.9	1.5	---	0	37.7	1.3	---
	50	105.6	1.9	97.4	100	136.5	1.8	98.8
Pb	0	86.4	1.5	---	0	83.9	1.7	---
	50	137.6	1.7	102.4	100	185.6	1.7	101.7
Zn	0	65.4	1.8	----	0	64.3	1.8	----
	50	116.4	1.9	102.2	100	165.8	1.7	101.5
Cu	0	84.4	1.4	----	0	89	1.6	----
	50	135.4	1.5	102.0	100	186.9	1.7	97.4

Table 5: Recovery of trace elements from blood and cow liver samples after application of the proposed CPE procedure ($N=3$)

Element	blood				Cow liver			
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	RSD%	Recovery %	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	RSD%	Recovery %
Ni	0	34.8	1.7	---	0	1.32	1.7	---
	50	85.4	1.5	101.2	5	6.53	1.3	104.2
Pb	0	31.8	1.9	---	0	1.21	1.7	---
	50	80.6	1.4	97.6	5	6.31	1.4	102.0
Zn	0	54.6	1.7	----	0	1.12	1.7	----
	50	104.8	1.5	100.4	5	6.17	1.2	101.0
Cu	0	78.5	1.9	----	0	6.85	0.9	----
	50	129.5	1.7	102.0	5	11.97	0.6	102.4

CONCLUSION

The micellar extraction of nickel, lead, zinc and copper ions with AMTD into the phase of non-ionic surfactant Triton X-114 has been investigated. The conditions for pre-concentration of metal ions were selected using model solutions. The accuracy and precision of the proposed CPE method was reported in terms of recovery (%) ranging from 98 to 100%, and R.S.D. (%) ranging from 1.2 to 1.7%. The detection limits of analyte ions investigated are superior to those of pre-concentration techniques for analyses (Elci *et al.* 2003, Hosseini *et al.* 2007). The proposed method can be applicable for the determination of trace metal ions in a variety of real samples with low detection limit, high accuracy and high precision compared with other methods.

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الطرق الوسطى المذيلة لتعيين العناصر الثقيلة في عينات حقيقية باستخدام طيف الامتصاص الذري اللهبى

فرشد أحمدى* و أزاده خان محمدى**
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خلاصة

لقد تم وصف طريقة بسيطة وحساسة لتعيين ما قبل التركيز باستخدام مستخلص النقطة الغيمية وطيف الامتصاص الذري اللهبى لاحقاً لتعيين أيونات النيكل، الرصاص، الزنك والنحاس في عينات حقيقية. عند الأس الهيدروجيني المتعادل تم استخدام "AMTD" وتريتون X - 114 كتدفق مائي عند سطح متأين. كما تم استخدام أعلى تركيز لكل من "AMTD" وتريتون X - 114 وحامض النيتريك والحمام المائي وسرعة ووقت قوة الطرد. لقد تم الحصول على الحدود الدنيا (3Sdb/m) ل 1.4، 1.6، 1.7 و 1.5 نانوجرام/لتر لكل من أيونات النيكل، الرصاص، الزنك والنحاس مع العامل التعزيزي 29. لقد تم تطبيق هذه الطريقة لتحديد المكونات في كبد البقر، المياه الطبيعية، ومياه الصرف الصناعي وعينات الدم وقد تم الحصول على نتائج ناجحة.