Regular Article

# Central Composite Design for the Optimization of Hydrogel Based pH-Dependent Extraction and Spectrophotometric Determination of Mercury

Sh. Jahangiri, M. Bahram\*, Kh. Farhadi and R. Hasanzadeh

*Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran*

In the present work a pH-dependent cloud point extraction procedure using pH-sensitive hydrogel polymer was applied for preconcentration and spectrophotometric determination of the Hg(II) as its Thio micher's ketone complex. Central composite design (CCD) and response surface method were applied to design the experiments and find out the optimum conditions. Four factors entitled concentration of hydrogel, HCl, TMK and KCl (to study the salting out effect) were investigated. At the optimum conditions, the analytical characteristics of the method (*e.g.*, limit of detection, linear range, Relative standard deviation) were obtained. Linearity was obeyed in the range of 5-200 ng ml$^{-1}$ of Hg(II) with a correlation coefficient of 0.987. The detection limit of the method was 1 ng ml$^{-1}$ for Hg(II) ion. Relative standard deviation (RSD) for 7 replicate determinations of complex mercury with Thio micher's ketone was 3.37%. The interference effect of some anions and cations was also investigated.

## INTRODUCTION

Most of heavy metal cations are extremely environmental pollutants because of their toxic effects on all living organisms. Among them, mercury is considered as one of the most hazardous metal ions for environment and has most commonly toxic risks for the contact of human environment as a result of natural processes, because it is widely distributed in water, air, and soil [1]. Hg(II), the most stable form of inorganic mercury, exists mostly in surface water due to its high water solubility. It makes several developmental delays and health problems which causes to damage the brain, nervous system, kidneys, endocrine system and leukemia [2]. Therefore, it is very important to be able to determine of trace amounts of mercury ions in biological and environmental samples with high sensitivity and selectivity. Past researches showed that the total mercury concentration in non-contaminated waters is ranging from 0.006 to 5 ng ml$^{-1}$ [3-5]. However, direct

_____
\*Corresponding author. E-mail: m.bahram@urmia.ac.ir

determination of trace level of mercury in environmental samples is not always simple. Various analytical methods such as atomic fluorescence spectrometry (AFS) [6], spectrometry [1,4,7], cold vapor atomic absorption spectrometry (CV-AAS) [5,8], inductively coupled plasma mass spectrometry (ICP-MS) [9], inductively coupled plasma-optical emission spectrometry (ICP-OES) [10], *etc.* have been reported in literature for determination and detection of mercury(II) ions. Spectrophotometer techniques are usually preferred, since they involve high sensitivity and provide low-cost instruments when appropriate chromogenic agents are available. Although, many reagents are used for the spectrophotometric measurement of mercury, their selectivity and sensitivity are not entirely satisfactory for determination of trace amount of mercury. 4,4-Bis (dimethylamino)thiobenzophenone (Thio-Michler's Ketone), was synthesized by Tarbell *et al*. in 1946. The sulfo dye functional group of this compound is selective to Hg(II) and is employed to determine trace amount of mercury(II) ions, Au, Pd, Pt [11,12]. Figure 1 shows the structure of ligand (TMK).

A number of methods have been suggested for pre-treatment and preconcentration of trace level of mercury. One of the classic pre-treatment techniques is liquid-liquid extraction (LLE). This method requires large amounts of toxic solvents. Endeavour research for novel sample pre-treatment methods has led to development of new techniques consisting of cold-induced aggregation microextraction (CIAME), dispersive liquid–liquid microextraction (DLLME), single drop microextraction (SDME), cloud point extraction (CPE), hollow fiber-liquid phase microextraction (HF-LPME), stir bar sorptive extraction (SBSE) and solid-phase microextraction (SPME) [13,4]. Main advantages of these methods are negligible volume of solvent consumed and high speed operation. Among these techniques, the cloud point extraction process is considered enormously superior to the other techniques. CPE is a low-cost, safe, rapid and simple technique with high recovery.

The important feature of CPE is the preferable use of water as a solvent in comparison with other pre-treatment techniques that still use hazardous and flammable organic solvents [15]. In recent years, CPE has been combined with a variety of instrumental techniques such as thermospray, flame furnace atomic absorption spectrometry (TS-FF-AAS) [16], chemiluminescence (CL), GF-AAS [17], flame atomic absorption spectrometry (FAAS) [18], gas chromatography (GC) [19], inductively coupled plasma optical emission spectrometry (ICP-OES) [20], tungsten coil electrothermal atomic absorption spectrometry (W-coil ET-AAS) [21,22], inductively coupled plasma mass spectrometry (ICP-MS) [23], capillary electrophoresis (CE) and high-performance liquid chromatography (HPLC) [24]. Recently, we [15] developed a novel and sensitive cloud point extraction procedure using pH-sensitive hydrogel for preconcentration and spectrophotometric determination of trace amounts of malachite green (MG). In this extraction method, appropriate amounts of poly (styrene-*alt*-maleic acid), as a pH-sensitive hydrogel, and HCl were added, respectively, into the aqueous sample so a cloudy solution was formed. The cloudy phase consisting of hydrogel particles distributed entirely into the aqueous phase. Organic or inorganic compounds having the potential to interact with polymer particles (chemical interaction or physical adsorption) could be extracted to cloudy phase.
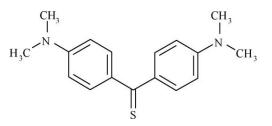


**Fig. 1.** struture of TMK.

In this paper, we develop an inexpensive, easy and fast method based on pH-sensitive polymers instead of conventional CPE method for preconcentration and spectrophotometric determination of Hg(II). The pH sensitive polymers are composed by adding pendant acidic or basic functional groups to the polymer backbone; these either accept or release protons in response to appropriate pH or ionic strength changes in aqueous media [25]. The procedure presented in this paper is based on the extraction of the formed mercury complex with TMK by pH-sensitive hydrogel. The extracted-rich phase is dissolved in methanol and its absorbance is measured by spectrophotometer. The effect of experimental parameters on the extraction efficiency including concentration of HCl and HG and TMK and KCl are investigated and optimized.

## EXPERIMENTAL

### Reagents and Solutions

All chemicals used in the experiments were of analytical grade and used without further purification. All solutions were prepared with double distilled water. HCl, KCl, Hg(NO$_3$)$_2$, TMK, methanol, ethanol and styrene, maleic anhydride, benzoyl peroxide, tetrahydrofuran, diethyl ether, NaOH were from Merck (Darmstadt, Germany). Hydrogel (0.4 g) was dissolved in 100 ml deionized water to obtain concentration of (0.4% w/v).

The stock solution of Hg(II) (1000 μg ml$^{-1}$) was prepared by dissolving known amounts of mercury salt in double distilled water. Stock solution of Thio-Michler's Ketone (1.1 × 10$^{-3}$ M) was prepared by dissolving the reagent in ethanol (Merck, Darmstadt, Germany). A buffer of pH = 3.5 was prepared by using sodium acetate (0.1 M) and hydrochloric acid (Merck, Darmstadt, Germany) at

appropriate concentrations.

Poly (styrene-*alt*-maleic acid) as an alternating copolymer (*alt*-PSMA) is a readily synthesized copolymer of styrene and maleic acid that incorporates two carboxylic groups and a phenyl group in each repeating unit. In *alt*-PSMA (120,000 average MW), the hydrophobic phenyl side group, contributed by the styrene unit, is directly attached to the hydrocarbon backbone. This compound derives its anionic charge from two free carboxyl groups (pKa 1.9 and 6.0) of maleic acid, which are also directly attached to the hydrocarbon backbone instead of the aromatic ring [26] and this compound is also commercially available (Sigma-Aldrich, Product no. 662631).

# PREPARATION OF POLY (STYRENE-*ALT*-MALEIC ACID)

Firstly, Poly (styrene-*alt*-maleic anhydride) (PSMA) was prepared through a thermally initiated free-radical polymerization of styrene and maleic anhydride according to the literature method [27].

## Apparatus

The spectrophotometric measurements were done using a double-beam, T80+ UV-Vis spectrophotometer PG (china) with a 1 cm quartz cell (volume 0.5 ml). For acceleration phase separation the Universal 320 centrifuge instrument (Hettich, Germany) was used.

## Statistical Software

Essential Regression and Experimental Design for chemists and Engineers (EREGRESS), as a MS Excel Add-in software [28] was used to design the experiments and to model and analyze the results.

## Extraction Procedure

10 ml of water sample containing suitable amount of mercury was placed in a 15 ml falcon tube and 0.7 ml hydrogel (0.4% w/v) was added. Then, 0.1 ml of acetate buffer (pH = 3.5) and 1 ml TMK ($1.1 \times 10^{-5}$ M) were added. After 10 min, 0.5 ml KCl and then 0.1 ml HCl (2 M) were added into the tube. The tubes were kept for 5 min in the room temperature before centrifugation. Separation of two phases was achieved by centrifugation for 10 min at 6000 rpm. The aqueous phase was then decanted. The sedimented phase was diluted with methanol and transferred into a 0.5 ml quartz cell to measure the absorbance of the solution at 570 nm against a reagent blank. Absorption spectra of TMK and its complex with mercury after cloud point extraction by hydrogel polymer are represented in Fig. 2.
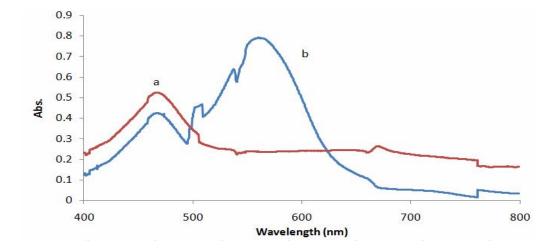


**Fig. 2.** Absorption spectra of (a) TMK and (b) its complex with mercury after cloud point extraction by hydrogel polymer.

## Central Composite Design

Central composite design (CCD) was used to design the experiment. The Central composite design determines an acceptable amount of information for testing well fitting and does not require an unusually large number of design points, thereby reduces the overall cost associated with the experiment. The response surface plots obtained through statistical process describes the design and the modeled CCD data. Response surface method graphically demonstrates the relationships between join of parameters and the response(s) and is the way to obtain an accurate optimum [28,29]. In order to obtain the optimum conditions, the effect of various parameters such as concentration of HCl, concentration of hydrogel (HG), concentration of Thio-Michler's Ketone (TMK) and salting out effect was taken account and the optimum conditions were chosen. In order to fit quadratic polynomials, the CCD combines a two-level factorial design with additional points (star points) and at least one point at the center of the experimental region to achieve properties such as rotatability or orthogonally. Four variables, namely, the concentration of HG ($F_1$), TMK ($F_2$), KCl ($F_3$) and HCl (F4) were investigated at five levels with four repeats at the central point. Polynomial equations, response surface, and central plots for a particular response were created using EREGRESS. The performance of the system was defined by the following quadratic Eq. (1):

$$Response = b_0 + b_1 \times F_1 + b_2 \times F_2 + b_3 \times F_3 + b_4 \times F_4 + b_5 \times F_1 \times F_1 + b_6 \times F_2 \times F_2 + b_7 \times F_3 \times F_3 + b_8 \times F_4 \times F_4 + b_9 \times F_1 \times F_2 + b_{10} \times F_1 \times F_3 + b_{11} \times F_1 \times F_4 + b_{12} \times F_2 \times F_3 + b_{13} \times F_2 \times F_4 + b_{14} \times F_3 \times F_4 \qquad (1)$$

Where $F_1$-$F_4$ are the 4 parameters, and $b_0$-$b_{14}$ are the coefficient values obtained through multiple linear regressions. For each of the four studied variables, high (coded value: +2) and low (coded: -2) set points were chosen to construct an orthogonal design as tabulated in Table 1. Also, Table 2 lists the coded values of designed experiments based on CCD.

## RESULT AND DISCUSSION

### Experimental Design

The purposes of this CCD design were: (1) investigation of the influence of concentration of hydrogel, concentration of HCl, concentration of TMK and salting out effect on the preconcentration and determination of mercury using pH-sensitive extraction; (2) recognition of the variables with highest effect on the extraction; and (3) finally displaying interactions between the variables. In order to find out the significant factors and build a model to optimize the procedure, a full quadratic model including all terms of Eq. (1) was constructed at the first step. Then, in order to obtain a simple and yet a realistic model, the insignificant terms were eliminated from the model through '*backward elimination*' procedure. By the elimination of non essential terms of Eq. (1) from the constructed model, calibration $R^2$ was decreased to 0.926, while adjusted $R^2$ ($R^2_{adj}$), and $R^2$ of prediction ($R^2_{pred}$) were increased to 0.895 and 0.829, respectively. The characteristics of the abstracted model including $R^2$ values, PRESS, standard error and significant linear, quadratic and interaction coefficients are shown in Table 3.

## Response Surface Method and Selection of the Optimum Conditions

To gain further insight about the influence of each variable, the three dimensional (3D) plots for the predicted responses were formed based on the model function. One of the response surface plots is describe and depicted in Fig. 3, which shows the 3D plots of absorbance of samples (570 nm) versus pairs of variables while the other variable was kept in the center levels. As shown in Fig. 3, there is a non-linear relation between the response and the variables. Using the response surfaces, the optimum conditions are attained and described in Table 4.

### Interference Studies

The effect of conventional coexisting ions on the determination of Hg(II) was studied. As seen in Table 5, most of the cations and anions have not interfered with the extraction and determination of mercury. Foreign ions were considered to interfere when their presence resulted in a variation in the absorbance of the sample of more than 5%. This increment of absorbance was evaluated at the wavelength of 570 nm (corresponding to maximum absorption of Hg complex). Results showed that $Ag^+$, $Au^{3+}$, $I^-$ and $Pd^{2+}$ can interfere in the extraction and determination

**Table 1.** The Variables and Values Used for Central Composite Design (CCD)

| Variable Name | | Coded factor levels | | | | |
|---|---|---|---|---|---|---|
| | | -2(low) | -1 | 0 | 1 | +2(high) |
| F1 | HG (%w/v) | 0.012 | 0.02 | 0.028 | 0.036 | 0.044 |
| F2 | TMK (mM) | 0.055 | 0.082 | 0.11 | 0.1375 | 0.165 |
| F3 | KCl (M) | 0 | 0.114 | 0.228 | 0.342 | 0.456 |
| F4 | HCl (M) | 0 | 0.01 | 0.02 | 0.03 | 0.04 |

**Table 2.** List of Experiments in the CCD (Coded Values) and the Response of each Run

| Design points | | | | | |
|---|---|---|---|---|---|
| | Factors | | | | |
| | F1 | F2 | F3 | F4 | Response |
| 1 | 0 | -1 | 0 | 0 | 0.134 |
| 2(cp) | 0 | 0 | 0 | 0 | 0.532 |
| 3 | 0 | 0 | -1 | 0 | 0.229 |
| 4 | 0 | 0 | 0 | 1 | 0.23 |
| 5(cp) | 0 | 0 | 0 | 0 | 0.445 |
| 6 | -0.5 | 0.5 | -0.5 | 0.5 | 0.387 |
| 7 | 0.5 | -0.5 | 0.5 | -0.5 | 0.124 |
| 8 | -0.5 | -0.5 | 0.5 | 0.5 | 0.253 |
| 9 | -0.5 | -0.5 | -0.5 | -0.5 | 0.193 |
| 10(cp) | 0 | 0 | 0 | 0 | 0.54 |
| 11(cp) | 0 | 0 | 0 | 0 | 0.494 |
| 12 | 0 | 1 | 0 | 0 | 0.26 |
| 13 | 0.5 | 0.5 | -0.5 | 0.5 | 0.186 |
| 14 | 0.5 | -0.5 | 0.5 | 0.5 | 0.452 |
| 15 | 1 | 0 | 0 | 0 | 0.369 |
| 16 | 0 | 0 | 0 | -1 | 0.003 |
| 17 | -0.5 | -0.5 | -0.5 | 0.5 | 0.39 |
| 18 | -0.5 | 0.5 | 0.5 | 0.5 | 0.32 |
| 19 | 0.5 | -0.5 | -0.5 | -0.5 | 0.069 |
| 20 | 0.5 | 0.5 | -0.5 | -0.5 | 0.116 |
| 21 | -1 | 0 | 0 | 0 | 0.46 |
| 22 | -0.5 | 0.5 | 0.5 | -0.5 | 0.141 |
| 23 | -0.5 | -0.5 | 0.5 | -0.5 | 0.112 |
| 24 | 0 | 0 | 1 | 0 | 0.187 |
| 25 | -0.5 | 0.5 | -0.5 | -0.5 | 0.196 |
| 26 | 0.5 | 0.5 | 0.5 | -0.5 | 0.26 |
| 27 | 0.5 | -0.5 | -0.5 | 0.5 | 0.197 |
| 28 | 0.5 | 0.5 | 0.5 | 0.5 | 0.31 |

(cp) indicates 4 repeat of the center point.

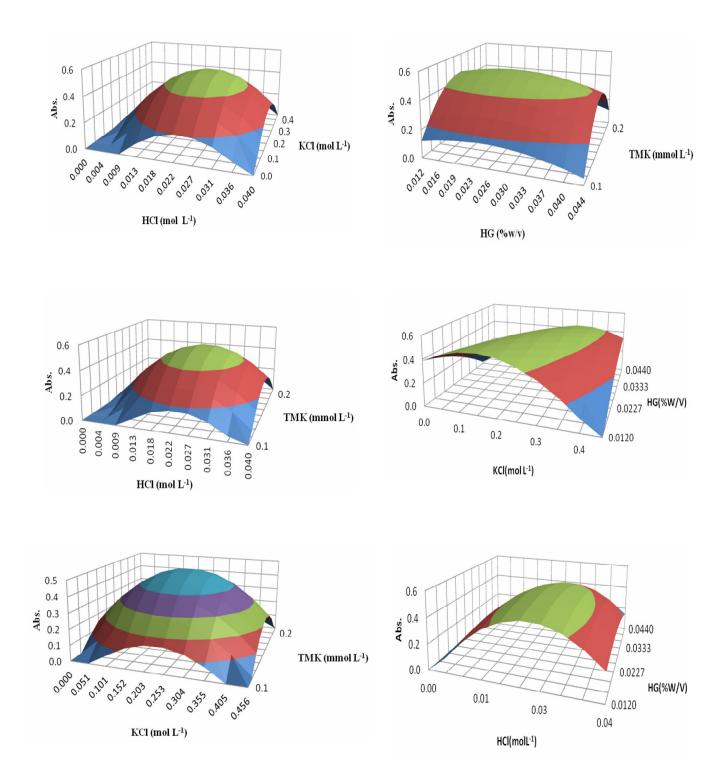**Table 3.** Some Characteristics of the Constructed Models

| Regression equation | | Coefficient | Value |
|---|---|---|---|
| Resp = b0 + b1*TMK_(mM) + b2*KCl_(M) + b3*HCL_(M) + b4*HG_(M)*HG_(M) + b5*HG_(M)*KCl_(M) + b6*TMK_(mM)*TMK_(mM) + b7*KCl_(M)*KCl_(M) + b8*HCL_(M)*HCL | | $B_0$ | -1.379 |
| | | $B_1$ | 22.71 |
| | | $B_2$ | 0.830 |
| \|R\| | 0.962 | $B_3$ | 45.73 |
| $R^2$ | 0.926 | $B_4$ | -305.42 |
| $R^2$ adjusted | 0.895 | $B_5$ | 64.28 |
| Standard Error | 0.04775 | $B_6$ | -100.64 |
| Points No. | 28 | $B_7$ | -5.644 |
| PRESS | 0.1 | $B_8$ | -962.30 |
| $R^2$ for Prediction | | 0.829 | |

**Table 4.** Optimum Conditions Obtained by Response Surface Modeling

| Variable name | Optimum values | Selected values |
|---|---|---|
| F1  HG (%w/v) | 0.0227-0.033 | 0.028 |
| F2  TMK(mM) | 0.1-0.2 | 0.11 |
| F3  KCl (M) | 0.152-0.355 | 0.228 |
| F4   HCl (M) | 0.018-0.036 | 0.02 |

**Table 5.** Effect of Foreign Ions on the Recovery of Mercury (50 ng ml$^{-1}$)

| Coexisting ion | Ion/Hg(II) ratio | Relative recovery (%) |
|---|---|---|
| $K^+$ | 1000 | 108 |
| $Na^+$ | 1000 | 107 |
| $Al^{3+}$ | 1000 | 100.6 |
| $Cr^{3+}$ | 1000 | 104.5 |
| $Mn^{2+}$ | 1000 | 95.9 |
| $Ni^{2+}$ | 1000 | 101.8 |
| $Pb^{2+}$ | 1000 | 101.9 |
| $Zn^{2+}$ | 1000 | 103.4 |
| $Co^{2+}$ | 1000 | 99.6 |
| $Cd^{2+}$ | 1000 | 99.9 |
| $Fe^{2+}$ | 1000 | 98.1 |
| $Mg^{2+}$ | 1000 | 98.2 |
| $Ca^{2+}$ | 1000 | 100.8 |
| $Cu^{2+}$ | 100 | 106.4 |
| $Fe^{3+}$ | 50 | 105.5 |
| $Cr^{6+}$ | 50 | 34.5 |
| $Pt^{4+}$ | 10 | 71.4 |
| $Ag^+$ | 1 | 133.9 |
| $Au^{3+}$ | 1 | 107.2 |
| $Pd^{2+}$ | 1 | 93.4 |
| $SO_4^{2-}$ | 1 | 97.6 |
| $PO_4^{3-}$ | 1000 | 98.1 |
| $Cl^-$ | 1000 | 98.7 |
| $F^-$ | 1000 | 100.4 |
| $NO_2^-$ | 10 | 101.1 |
| $I^-$ | 1 | 93.6 |

**Fig. 3.** Response surfaces.

of Hg(II) ions at a higher concentration levels. $NO_2^-$ had unfavorable effect on the absorbance at the concentration of 10 times more than that of mercury. Since commonly present ions in water samples did not have significant effect on the recovery of Hg(II), consequently the method can be employed to determine Hg(II) in environmental water samples.

## Analytical Characteristics

Table 6 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, detection limit, reproducibility, preconcentration, and improvement factors. The limit of detection, defined as $C_{LOD} = 3S_B/m$ (where $S_B$ and $m$ are standard deviation of the blank and slope of the calibration graph, respectively) was 1 ng $ml^{-1}$. Since the amount of mercury in 10 ml of initial sample solution is measured after preconcentration by pH-sensitive hydrogel extraction in a final volume of 0.5 ml (0.2 ml hydrogel rich-phase + 0.3 ml metanol), the solution was concentrated by a factor of 20. The improvement factor, defined as the ratio of the slope of the calibration graph for the pH-sensitive hydrogel extraction method to the slope of the calibration graph in the presence of hydrogel without preconcentration was 21.

## Application of the Proposed Method

The proposed method was employed to the determination of Hg(II) in several spiked water samples.

**Table 6.** Analytical Characteristics of the Proposed Method

| | |
|---|---|
| Regression equation[a] | Abs = 2.101C+0.013 |
| $R^{2}$[b] | 0.987 |
| Linear range (ng $ml^{-1}$) | 5-200 |
| LOD (ng $ml^{-1}$)[d] | 1 |
| Repeatability (RSD)[c] | 3.37% |
| Regression equation before extraction[a] | Abs = 0.098C+ 0.010 |
| Concentration factor | 20 |
| Improvement factor[e] | 21 |

[a]Concentration of mercury (C/mg $l^{-1}$). [b]Squared regression coefficient. [c]Relative standard deviation for 6 replicate determination of 50 ng $ml^{-1}$ Hg(II). [d]LOD, limit of detection for S/N = 3. [e]The ratio of the slope of the calibration graph for the pH-sensitive hydrogel extraction method to that of the slope of the calibration graph without preconcentration

**Table 7.** Determination of Mercury in the Water Samples by Proposed Method (ng $ml^{-1}$)

| Sample | Added (ng $ml^{-1}$) | Found (ng $ml^{-1}$) | Recovery (%) |
|---|---|---|---|
| Aras river water1 | 40 | 41 | 102.5 |
| Aras river water1 | 45 | 46 | 102.2 |
| mineral water2 | 50 | 49 | 98 |
| mineral water2 | 55 | 53 | 96.3 |

The results are presented in Table 7. The recoveries are close to 100% indicating that the method has been helpful for the preconcentration and determination purposes.

## CONCLUSIONS

In this work, for the first time, pH-sensitive hydrogel based CPE was applied for preconcentration and determination of a metallic cation, *e.g.* Hg(II). The proposed method is very simple and rapid. Instruments used are low cost and easy to operate. This procedure has high preconcentration abilities. The presented cloud point extraction based on hydrogel is more eco-friendly. In comparison to traditional CPE, this new method avoids the heating and cooling processes. By using pH-sensitive hydrogel extraction, toxic solvent extraction is avoided too. Central composite design was applied to design the experiments and response surface was used to acquire the optimum conditions.

## REFERENCES

[1] A. Niazi, T. Momeni-Isfahani, Z. Ahmari, J. Hazard. Mater. 165 (2009) 1200.

[2] Y. Wang, F. Yang, X. Yang, Biosens. Bioelectron. 25 (2010) 1994.

[3] C. Huang, B. Hu, Spectrochim. Acta Part B 63 (2008) 437.

[4] M. Baghdadi, F. Shemirani, Anal. Chim. Acta 613 (2008) 56.

[5] N. Pourreza, K. Ghanemi, J. Hazard. Mater. 161 (2009) 982.

[6] M. Tuzen, M. Soylak, Bull. Environ. Contam. Toxicol. 74 (2005) 968.

[7] J. Fan, Y. Qin, C. Ye, P. Peng, C. Wu, J. Hazard. Mater. 150 (2008) 343.

[8] M. Tuzen, M. Soylak, Bull. Environ. Contam. Toxicol. 74 (2005) 968.

[9] J. Chen, H. Chen, X. Jin, H. Chen, Talanta 77 (2009) 1381.

[10] J.C.A. de Wuilloud, R.G. Wuilloud, M.F. Silva, R.A. Olsina, L.D. Martinez, Spectrochim. Acta Part B 57 (2002) 365.

[11] K.L. Cheng, B.L. Goydish, J. Microchem. 10 (1996) 158.

[12] B. Di, H. Xiangying, G. Ridi, *et al.* Gold 23 (2002) 47.

[13] N. Ferrus, S. Cerutti, J.A. Salonia, L.D. Martinez, J. Hazard. Mater. 141 (2007) 693.

[14] B.K. Priya, P. Subrahmanayam, K. Suvardhan, K.S. Kumar, D. Rekha, A.V. Rao, G.C. Rao, P. Chiranjeevi, J. Hazard. Mater. 144 (2007) 152.

[15] M. Bahram, F. Keshvari, P. Najafi-Moghaddam, Talanta 85 (2011) 891.

[16] P. Wu, Y.C. Zhang, Y. Lv, X.D. Hou, Spectrochim. Acta Part B 61 (2006) 1310.

[17] T.D.A. Maranhao, D.L.G. Borges, M.A.M.S. da Veiga, Spectrochim. Acta Part B 60 (2005) 667.

[18] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, J. Hazard. Mater. 168 (2009) 1022.

[19] T.I. Sikalos, E.K. Paleologos, Anal. Chem. 77 (2005) 2544.

[20] Y.J. Li, B. Hu, Z.C. Jiang, Anal. Chim. Acta 576 (2006) 207.

[21] G.L. Donati, K.E. Pharr, P.C. Calloway Jr., J.A. Nobrega, B.T. Jones, Talanta 76 (2008) 1252.

[22] X.D. Wen, P. Wu, L. Chen, X.D. Hou, Anal. Chim. Acta 650 (2009) 33.

[23] R.A. Gil, J.A. Gⅎsquez, R. Olsina, L.D. Martinez, S. Cerutti, Talanta 76 (2008) 669.

[24] J. Lopez-Darias, V. Pino, J.H. Ayala, V. Gonzalez, A.M. Afonso, Anal. Bioanal. Chem. 391 (2008) 735.

[25] A.K. Bajpai, S.K. Shukla, S. Bhanu, S. Kankane, Progr. Polym. Sci. 33 (2008) 1088.

[26] S. Srivastava, R. Sinha, D. Roy, Aquat. Toxicol. 66 (2004) 319.

[27] A. Stammati, C. Nebbia, I.D. Angelis, A.G. Albo, M. Carltti, C. Rebecchi, F. Zampaglioni, M. Dacasto, Toxicol. In Vitro 19 (2005) 853.

[28] D.D. Stephan, J. Werner, R.P. Yeater, Essential Regression and Experimental Design for Chemists and Engineers, MS Excel Add in Software Package, 1998-2001.

[29] I. Bulacov, J. Jirkovsky, M. Muller, R.B. Heimann, Surf. Coat. Technol 201 (2006) 255.