Selective Pre-concentration and Solid Phase Extraction of Mercury(II) from Natural Water by Alumina-Loaded 2-(2-Quinolylazo)-5-diethylamino Benzoic Acid Phases

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Alumina phase loaded with 2-(2-quinolylazo)-5-diethyl-amino benzoic acid were synthesized based on chemical binding and physical adsorption approaches. The stability of a chemically modified 2-(2-quinolylazo)-5-diethylamino benzoic acid especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of alumina immobilized 2-(2-quinolylazo)-5-diethyl-amino benzoic acid. The application of this alumina for sorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. This difference was interpreted on the basis of selectivity incorporated in these sulfur containing alumina phases. Hg(II) was found to exhibit the highest affinity towards extraction by these alumina phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for Hg(II) to occur by alumina immobilized 2-(2-quinolylazo)-5-diethylamino benzoic acid. The potential applications of alumina immobilized 2-(2-quinolylazo)-5-diethylamino benzoic acid for selective extraction of mercury(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Hg(II) (45 pg mL^{-1}) from natural tap water with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapour atomic absorption analysis.

Key Words: Solid phase extraction, Mercury(II), Alumina, 2-(2-Quinolylazo)-5-diethylamino benzoic acid.

INTRODUCTION

The direct determination of trace metals especially toxic metal ions such as mercury, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step[1].

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This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest[2]. This can be performed simply in many ways including liquid and solid phase extraction techniques[3,4]. The application of solid phase extraction technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form[5].

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams[6], filter paper[7], cellulose[8] and ion exchange resins[9]. Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces[10] of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports[11]. The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes[12]. For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters[13]. Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place[10].

Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds[14-18]. The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of mercury(II)[19,20] and pre-concentration of various cations[21-26] and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations[27].

This paper reported the applications of alumina phase-impregnated with 2-(2-quinolylazo)-5-diethylamino benzoic acid for selective extraction and solid phase pre-concentration of mercury(II) from aqueous and natural water samples.

EXPERIMENTAL

Analytical grade metal(II) nitrate salts and alumina used were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstat, Germany and double distilled deionized water was used throughout the experiments. 3-Chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. For all solutions, double distilled water was used and the buffer solutions were prepared from 1 M sodium acetate to which different volumes of 1 M hydrochloric acid were mixed and the pH-value of the resulting solution was adjusted with the use of a pH-meter.

2-(2-Quinolylazo)-5-diethylamino benzoic acid (QADEAB) was prepared as described[26].

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of alumina loaded-2-(2-quinolylazo)-5-diethylamino benzoic acid were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except mercury(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Mercury(II) determinations were performed at Varian Spect AA-10 plus atomic absorption spectrophotometer equipped with VGA-76 vapour generation.

Preparation of alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phases: Activation of surface alumina was filtered, washed with toluene, ethanol and diethyl ether and finally dried in an oven at 70 °C for 6 h. An amount of 20 g of dry alumina were added to 5.12 g (20 mmol) 2-(2-quinolylazo)-5-diethylamino benzoic acid already dissolved in 400 mL dry and hot toluene in the presence of a few drops of pyridine and the reaction mixture was refluxed for 6 h. The resulting phase was filtered, washed with toluene, ethanol and finally with water several times until the filtrate showed no characteristic colour of adsorbed 2-(2-quinolylazo)-5-diethylamino benzoic acid. The phase was then dried in an oven at 60 °C for 7 h alumina physically adsorbed 2-(2-quinolylazo)-5-diethylamino benzoic acid phase was prepared by reflux of 20 g of active alumina and 10.12 g of 2-(2-quinolylazo)-5-diethylamino benzoic acid in 400 mL toluene for 6 h. Phase was also washed and dried as mentioned above.

Stability studies: The stability of alumina phases in different buffer solutions (pH 1-6) and concentrated hydrochloric and nitric acids was studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 mL of the selected solution in 100 mL measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 mL water and dried in an oven at 80 °C. Around 100 mg of the treated phase was added to 10 mL of mercury(II) (0.1 M) and 9 mL of sodium acetate (0.1 M)

and the mixture was shaken for 0.5 h by an automatic shaker. The percentage of hydrolysis of 2-(2-quinolylazo)-5-diethylamino benzoic acid from the surface of modified alumina phases in different acidic solutions was calculated from the determined $\mu mol\ g^{-1}$ value of each treated phase.

Sorption studies

Determination of $\mu mol\ g^{-1}$ values: The determination of metal capacity of 13 metal ions, *viz.*, Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ba(II), Hg(II) and Pb(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1 mL of metal ion (0.1 M) and 9 mL of the buffer solution (pH 1-6 and 0.1 M sodium acetate) in 50 mL measuring flask. The mixture was then automatically shaken for 0.5 h, filtered, washed with 50 mL of water. The unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Hg(II) by the static technique. In this, 100 mg of the alumina phase was added to 1 mL of Hg(II) (0.1 M) and 9 mL of sodium acetate (0.1 M) in 50 mL measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20 and 25 min). The mixture was filtered, washed with 50 mL of water and the free metal ion was determined as described above.

Determination of the distribution coefficient: About 100 mg of the alumina phase was mixed with 50 mL of the metal ion (1 mg mL^{-1}) in a 100 mL measuring flask and shaken for 3 h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2 % nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

Percentage removal of mercury(II) from aqueous solutions: 1 L of Hg(II) solution, containing 10, 50 and 100 ng mL^{-1} was passed over a column packed with 500 and 1000 mg each of alumina. The flow rate was adjusted to 2 mL min^{-1}. The eluents were collected and 5 mL was diluted with 20 mL of nitric acid solution (2 %) and subjected to cold vapour atomic absorption spectrometric analysis (CV-AAS).

Pre-concentration of Hg(II) from aqueous and natural tap water: 2 L sample solution spiked with 20 pg mL^{-1} in both double distilled water and natural tap water were prepared and passed over a column packed with 1000 mg of alumina with a flow rate of 2 mL min^{-1}. Then 10 mL concentrated hydrochloric acid (10 M) was then passed over the phase and adsorbed metal ion to desorb the bound-mercury(II). The desorbed metal ion was directly determined by CV-AAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

RESULTS AND DISCUSSION

Metal capacity in various controlling factors: The metal capacity values determined in μmol g^{-1} for the alumina phase-loaded- 2-(2-quinolyl-azo)-5-diethylamino benzoic acid in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the alumina phase. Table-1 compiles the μmol g^{-1} values for the 13 tested metal ions, *viz.*, Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II),Cd(II), Hg(II) and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of μmol g^{-1} extracted values from the metal ion solution for most tested metal ions on the pH-value[20,24].

TABLE-1
METAL CAPACITY VALUES DETERMINED IN μmol g^{-1}*

pH	Hg(II)	Pb(II)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
NaOAc	262	53	55	22	–	80	45	66	15	45
6	213	45	36	54	5	129	63	97	37	64
5	135	32	24	63	12	140	66	70	22	36
4	56	25	15	51	47	91	36	68	15	30
3	35	16	15	29	34	45	38	40	8	18
2	24	8	5	19	26	38	21	26	00	6
1	12	3	3	13	6	22	14	15	00	00

*Values are based on n = 3 with standard deviation of 4.

The maximum value was found to be mainly at higher pH-values (pH 5-6 and 0.10 M NaOAc). Second, is the strong affinity of the alumina phase for extraction and removal of Hg(II) from aqueous solution compared to other tested metal ions, as shown by the higher μmol g^{-1} values by alumina phases 250.

This behaviour of alumina-loaded sulfur containing compounds for selective extraction and removal of Hg(II) from aqueous and natural water sample is well documented[19,20] and reported based on different governing rules[17]. Third are the notably high μmol g^{-1} values determined for chemically modified alumina phase in comparison with values found as given in Table-1. The comparison between the metal sorption properties of chemically and physically-alumina phases has been extensively studied[21] and the results presented in this work are consistent with the surface activity of the donor atoms responsible for metal ion interaction, sorption, extraction and selective removal. In the case of the physically adsorbed phase, some of these donor atoms are involved in physical adsorption processes with the active surface, leading to the minimization of the reactivity of such donor atoms

for metal interaction and binding processes. In contrast, the chemical binding of 2-(2-quinolylazo)-5-diethylamino benzoic acid was accomplished *via* direct bond formation between silica modified propylchloride with the thiol- or imino-group[9]. The product, alumina, in this case is tuned with the active donor atoms (N) directed on the surface of the modified silica gel with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, are the general orders of metal capacity values for all tested metal ions by the two phases which are in many respects consistent and similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Hg(II) as well as the higher metal uptake behaviour of alumina phase.

Stability studies: The stability of the newly synthesized alumina phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the alumina phase[14]. The results of this study proved that the alumina-chemically immobilized 2-(2-quinolyl-azo)-5-diethylamino benzoic acid phase is more resistant than the physically adsorbed analog especially in 1, 5 and 10 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

However, the use of nitric acid with different concentration values (1, 5, 10 M) was found to change the colour of alumina phases from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic 2-(2-quinolylazo)-5-diethylamino benzoic acid modifier *via* oxidation. In addition, stability of phases was also confirmed from the interaction with 10 M hydrochloric acid for more than 1 week.

This test proved a reasonable stability of alumina phase compared to non-treated silica gel phases judging from the colour change of the two phases as well as the metal capacity values determination of Hg(II) and comparison of these with those of the original non-treated alumina phases. Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a polymeric matrix[9]. Finally, the alumina phase-loaded 2-(2-quinolyl-azo)-5-diethylamino benzoic acid phases were also found to be stable over a range of 1 year during the course of this work.

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as μmol g^{-1} and correlated to that determined at 0.5 h

shaking time. Fig. 1 represents the percentage extraction *vs.* shaking time in min and clearly reflects the rapid exchange equilibrium between alumina phase and Hg(II). One minute shaking time was found to be sufficient to establish 84 % of the determined μmol g^{-1} value at 0.5 h whereas 10 min shaking time led to 98 % extraction. The data and results presented reveal the superiority of alumina phase as previously declared in the stability studies.
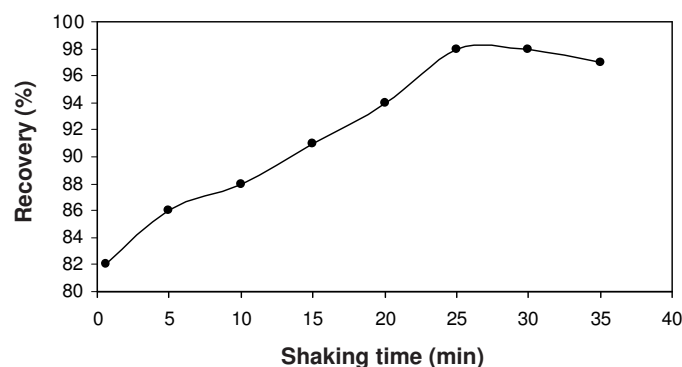

Fig. 1.   Effect of shaking time (min) on the percentage extraction of Hg(II) by the alumina phases

The distribution coefficient (K_d) data of the tested metal ions with the two newly alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase are summarized in Table-2. It is evident that Hg(II) is the strongest sorbed metal ion by alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase. The distribution coefficient values of Hg(II) by the loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase were found to be much higher than those reported for ion exchange resins containing 2-(2-quinolylazo)-5-diethylamino benzoic acid derivatives[9]. In addition, the K_d values for Cu(II) by alumina-loaded 2-(2-quinolylazo)-5-diethyl-amino benzoic acid phase were found to come on the second place after Hg(II) which behaviour can be interpreted on the basis of the affinity of both nitrogen and sulfur donor atoms present in 2-(2-quinolylazo)-5-diethyl-amino benzoic acid for binding with Cu(II)[19,20]. On the other hand, the various tested metal ions as shown in Table-2 were found to exhibit lower tendency to bind with alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Hg(II) and the lower ones for the other metal ions, except Cu(II), provide an additional evidence for the suitability of these two newly alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase for selective extraction of Hg(II) from aqueous solutions.

TABLE-2
DISTRIBUTION COEFFICIENT (K_d) VALUES OF VARIOUS METAL IONS

Metal ions	K_d	Metal ions	K_d
Cr(III)	169	Cu(II)	713
Mn(II)	95	Zn(II)	442
Fe(III)	75	Cd(II)	118
Co(II)	590	Hg(II)	14000
Ni(II)	65	Pb(II)	168

Percentage removal of Hg(II) from aqueous solution: In this study, an attempt was made to evaluate the percentage recovery of Hg(II) with different spiked concentrations, namely 10, 50 and 100 ng mL^{-1} from 1 L of NaOAc solution (0.1 M) by the application of two different amounts (500 and 1000 mg) of alumina-loaded 2-(2-quinolylazo)-5-diethylamino benzoic acid phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in Table-3, which clearly demonstrate the suitability and validity of alumina immobilized 2-(2-quinolylazo)-5-diethylamino benzoic acid phase for removal and extraction of Hg(II). In addition, the effect of packing amount of silica gel phase is also evident in Table-3, where the near completion of Hg(II) removal was accomplished by the use of 1000 mg phase.

TABLE-3
PERCENTAGE REMOVAL OF Hg(II) FROM AQUEOUS SOLUTIONS BY
ALUMINA-LOADED 2-(2-QUINOLY LAZO)-5-DIETHYLAMINO
BENZOIC ACID PHASE*

Hg(II) spiked (ng mL^{-1})	Phase (mg)	Percentage removal	Hg(II) spiked (ng mL^{-1})	Phase (mg)	Percentage removal
10	500	94 ± 0.6	10	1000	100 ± 1.7
50	500	96 ± 2.0	50	1000	97 ± 1.9
100	500	94 ± 2.0	100	1000	98 ± 1.5

*Values are based on triplicate analysis.

Selective pre-concentration of Hg(II) from natural water for off-line CV-AAS: This study was undertaken in order to evaluate the potential application of alumina immobilized 2-(2-quinolylazo)-5-diethylamino benzoic acid phase for pre-concentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water to evaluate and investigate the matrix effect. Both drinking tap water and double distilled water (2 L) were spiked with 20 pg mL^{-1} of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal

ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl[9] as well as ethylenediaminetetra acetic acid[24]. However, some of these reagents are usually characterized by adsorption on the surface of alumina which lead to severe change in the nature of packing material as well as non reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Hg(II) by 10 M HCl acid is found to be high without causing any notable change to the chemical nature of the organic 2-(2-quinolylazo)-5-diethylamino benzoic acid modifier. Therefore, 10 mL of HCl (10 M) was used for the elution of the adsorbed Hg(II) from the column bed. The pre-concentration factor targeted from this study is 200 as given in Table-4. As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory pre-concentration factor which can be further increased to 500-fold by simply increasing the water sample volume to 5 L instead of 2 L. Moreover, natural tap water sample was found to give very close results to that reported for double distilled water sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed selective extraction, removal and pre-concentration of Hg(II) by alumina immobilized 2-(2-quinolylazo)-5-diethylamino benzoic acid phase.

TABLE-4
PRECONCENTRATION OF Hg(II) FROM DDW AND
NATURAL TAP WATER SAMPLES*

Phase (mg)	Sample volume (mL)	Hg(II) spiked (pg mL^{-1})	Preconcen-tration reagent	Preconcen-tration factor	Hg(II) detected* (ng mL^{-1})	Percentage removal
1000	2000 tap water (Saveh)	20	10 mL of 10 M HCl	200	3.98±2.3	99.6±1.5
1000	2000 DDW	20	10 mL of 10 M HCl	200	3.98±2.2	98.9±2.1

*Values are corrected for blank concentration of water samples and based on triplicate analysis. DDW = Double distilled water.

REFERENCES

1. D.E. Leyden, G.H. Luttrell, W.K. Nonidez and D.B. Werho, *Anal. Chem.*, **48**, 67 (1976).
2. J.S. Jones, D.E. Harrington, B.A. Leone and W.R. Bramdstedt, *Atom. Spectrosc.*, **4**, 49 (1983).
3. D.C. Nambiar, N.N. Patil and V.M. Shinde, *Fresenius J. Anal. Chem.*, **360**, 205 (1998).
4. C. Caroli, A. Alimanti, F. Petrucci and Zs. Horvath, *Anal. Chim. Acta*, **248**, 241 (1991).
5. A. Alexandrova and S. Arpadjan, *Analyst*, **118**, 1309 (1993).
6. S. Arpadjan, L. Vuchkova and E. Kostadinova, *Analyst*, **122**, 243 (1997).
7. D.E. Leyden and G.H. Luttrell, *Anal. Chim.*, **47**, 1612 (1975).

8.   M.C. Gennaro, C. Baiocchi, E. Campi, E. Mentasti and R. Aruga, *Anal. Chim. Acta*, **151**, 339 (1983).
9.   M. Grote and A. Kettrup, *Anal. Chim. Acta*, **175**, 239 (1985).
10. K. Unger, Porous Silica, Elsevier, Amsterdam (1979).
11. S.P. Boudreau and W.T. Cooper, *Anal. Chem.*, **61**, 41 (1989).
12. R.J. Kvitek, J.F. Evans and P.W. Carr, *Anal. Chim. Acta*, **144**, 93 (1982).
13. M.L. Bruening, D.M. Mitchell, J.S. Bradshaw, R.M. Izatt and R.L. Bruening, *Anal. Chem.*, **63**, 21 (1991).
14. M.E. Mahmoud, *Talanta*, **45**, 309 (1997).
15. M.E. Mahmoud and E.M. Soliman, *Talanta*, **44**, 15 (1997).
16. M.E. Mahmoud and E.M. Soliman, *Talanta*, **44**, 1063 (1997).
17. A. Tong, Y. Akama and S. Tanaka, *Anal. Chim. Acta*, **230**, 179 (1990).
18. V. Dadler, L.F. Lindoy, D. Sallin and C.W. Schlaepfer, *Aust. J. Chem.*, **40**, 1557 (1987).
19. M.E. Mahmoud, in: Proceeding of the 25th FACSS Conference, Austin, TX, USA, 11-15 October (1998).
20. M.E. Mahmoud, *Anal. Chim. Acta*, **398**, 297 (1999).
21. D.E. Leyden, G.H. Luttrell, A.E. Sloan and N.J. DeAngelis, *Anal. Chim. Acta*, **84**, 97 (1976).
22. A. Moghimi, *Chin. J. Chem.*, **25**, 640 (2007).
23. A. Moghimi, M.S. Tehrani and S.W. Husain, *Mater. Sci. Res. (India)*, **3**, 27 (2006).
24. M.S. Tehrani, A. Moghimi and S.W. Husain, *Mater. Sci. Res. (India)*, **3**, 135 (2006).
25. Q.F. Hu, G.Y. Yang, D.Y. Tang and J.Y. Yin, *Chin. J. Arid Environ. Monit.*, **15**, 196 (2001).
26. P. Nayebi and A. Moghimi, *Mater. Sci. Res. (India)*, **3**, 179 (2006).
27. P. Qiaosheng, S. Qiaoyu, H. Zhide and S. Zhixing, *Analyst*, **123**, 239 (1998).