# Poly[1-(N,N-*bis*-carboxymethyl)amino-3-allylglycerol-*co*-dimethylacrylamide] brushes grafted onto siliceous support for preconcentration and determination of cobalt (II) in human plasma and environmental samples

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**Abstract**−A chelating matrix prepared by surface grafting of polymer containing a functional monomer, poly[1-(N,N-*bis*-carboxymethyl)amino-3-allylglycerol-*co*-methylacrylamide] (poly(AGE/IDA-co-DMAA) onto a modified silica. The silica surface was modified by silylation with 3-mercaptopropyltrimethoxysilane followed by graft polymerization. Monomer of allyl glycidyl ether-iminodiacetic acid was synthesized by reaction of allyl glycidyl ether with iminodiacetic acid. The chelating sorbent can be reused for 15 cycles of sorption-desorption without any significant change in sorption capacity. The profile of cobalt uptake on the sorbent reflects good accessibility of chelating sites in poly(AGE/IDA-co-DMAA)-grafted silica gel. The equilibrium adsorption data of Co(II) on modified sorbent were analyzed by Langmuir, Freundlich, Temkin and Redlich-Peterson models. The method was applied for cobalt ions determination in human plasma and sea water sample with satisfactory results.

Key words: Solid Phase Extraction, Polymer Grafting, Cobalt, Isotherm Study, Preconcentration

## INTRODUCTION

Cobalt is an essential element at trace level to humans, animals and plants for metabolic processes. It helps to repair the myelin sheath, pernicious anemia, and building of red blood cells. More attention has been focused on the toxicity of cobalt in large concentrations, since it has been found that cobalt can cause vasodilation, flushing and cardiomyopathy in humans and animals. It was reported that cobalt-mediated free radical generation contributes to interfere with DNA repair processes [1-3]. The International Agency for Research on Cancer (IARC) has classified this metal as possibly carcinogenic to humans [4].

Except occupational sources, the main sources of cobalt are foods and beverages. The World Health Organization (WHO) recommends that 0.005-0.010 mg of cobalt might be the daily optimal intake for adults [5]. Therefore, the determination of Co(II) in water, food, and environmental samples is important in the fields of environmental analysis and medicine.

Due to the allowable low levels of cobalt in food and beverages, and its very low concentrations in natural waters as described above, reliable and sensitive analytical methods are required for determination of this metal. For this purpose, preconcentration techniques in connection with analytical methods such as electrothermal atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry have been used [6-9]. The use of preconcentration techniques

in the determination of Co(II) by flame atomic absorption spectrometry (FAAS) is still important [10,11]. Among the preconcentration techniques, solid phase extraction (SPE) has received the most attention due to its simplicity, high concentration factor, and more environmentally friendly reagents used. Moreover, SPE and solvent extraction have also been used for speciation studies [12,13]. Surface modification by grafting polymer chains to solid substrates is a useful method for producing materials which possess specific surface and structural properties. Polymer grafting is the process of attaching living polymer chains to reactive sites on polymers [14] or other surfaces. Grafted polymers offer unique opportunities to tailor and manipulate interfacial properties while retaining the basic mechanical strength and geometry of the supporting solid substrate. Applications of polymer-grafted substrates include filler-polymer control in polymer composites, packings for liquid and gas chromatography, biocompatible surfaces, suspensions with colloid stability, and modified inorganic membranes. In particular, surface-grafted water-soluble polymers, which are of interest in this work, have been investigated for use as chromatographic resins [15-17].

The aim of this work is to show the analytical potentiality of poly (AGE/IDA-co-DMAA)-grafted silica gel for preconcentration/determination of Co(II) from aqueous solutions like biological fluid and environmental water samples following FAAS determinations. For this purpose, free-radical graft co-polymerization of N, N-dimethylacrylamide (DMAA) and a functional monomer containing metal chelating group, 1-(N,N-bis-carboxymethyl)amino-3-allylglycerol (AGE/IDA) onto silica surface modified with (3-mercaptopropyl)trimethoxy silane (MPTMS) was accomplished and then effects of some analytical conditions such as sample pH, contact time and

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matrix interferences were examined.

## EXPERIMENTAL SECTION

### 1. Instruments

Flame atomic absorption spectrometer Varian, (Palo Alto, CA, USA) AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L·min$^{-1}$, respectively) and Inductively coupled plasma-Atomic emission spectroscopy (ICP-AES), Varian, model Vista were used for concentration measurements of metal ions. The pH was measured with a Metrohm model 744 pH meter (Zofingen, Switzerland).

### 2. Reagents and Solutions

DMAA, MPTMS, and aluminum oxide were from Aldrich (Steinheim, Germany). 2, 2'-Azobis (2-methylpropionittrile) was purchased from Acros (New Jersey, USA). AGE was purchased from Fluka Chemical (Buchs Switzerland). Anhydrous 1,4-Dioxane, silica gel 60 for column chromatography (0.2-0.5 mm), IDA, NaOH, HCl, H$_2$SO$_4$, HNO$_3$, NaOH, K$_2$SO$_4$, NaCl, CH$_3$COOH, CH$_3$COONa, Na H$_2$PO$_4$, Na$_2$HPO$_4$, Pb(NO$_3$)$_2$, FeSO$_4$·7H$_2$O, CuSO$_4$·5H$_2$O, Co(NO$_3$)$_2$· 6H$_2$O, Ni SO$_4$·6H$_2$O, Zn SO$_4$·7H$_2$O, Hg(NO$_3$), Al(NO$_3$)$_3$, Ag(NO$_3$), Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Ba(NO$_3$)$_2$ and C$_2$H$_5$OH were products of Merck (Darmstadt, Germany).

All the reagents were of analytical grade and used without any further purification.

The stock solution (1,000 mg·L$^{-1}$) of Co(II) was prepared by dissolving appropriate amounts of Co(NO$_3$)$_2$ in deionized water. To adjust the pH of the solution, 10 mL of 0.1 M acetic acid - acetate buffer (pH 3-6.5) or 0.01 M phosphate buffer (pH 6.5-9) was used wherever suitable.

### 3. Synthesis of Poly(AGE/IDA-co-DMAA)-grafted Silica Gel

Details of the preparation and characterization of the poly[1-(N,N-bis-carboxymethyl)amino-3-allylglycerol-codimethylacrylamide] (poly(AGE/IDA-co-DMAA)-grafted silica gel) were reported in the previous work [18]. First, coupling of AGE with IDA as the chelating monomer, then modification of silica with MPTMS should be done. Finally, the free radical graft copolymerization of AGE/IDA and DMAA-onto modified silica particles was carried out in a temperature-controlled reactor with vigorous stirring under a nitrogen atmosphere. The methodology used to synthesize of poly(AGE/IDA-co-DMAA)-grafted silica gel is summarized in Fig. 1.

### 4. Batch Method of Co(II) Adsorption

A set of solutions (the volume of each 100 mL) containing 0.5 μg·mL$^{-1}$ of Co(II) was taken. Their pH values were adjusted between the ranges 3-9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.05 g of poly(AGE/IDA-co-DMAA)-grafted silica gel was added to each solution and the mixture was shaken for 4 h. The sorbent was filtered and the adsorbed metal ions were eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by FAAS.

### 5. Co(II) Adsorption

Isotherm studies were conducted in a batch mode to determine the adsorption of Co(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel, using stoppered conical flasks. In these experiments, 100 mL of Co solution with a Co concentration varying from 10 to 100 mg L$^{-1}$, was poured into each flask to which 0.1 g of poly(AGE/IDA-
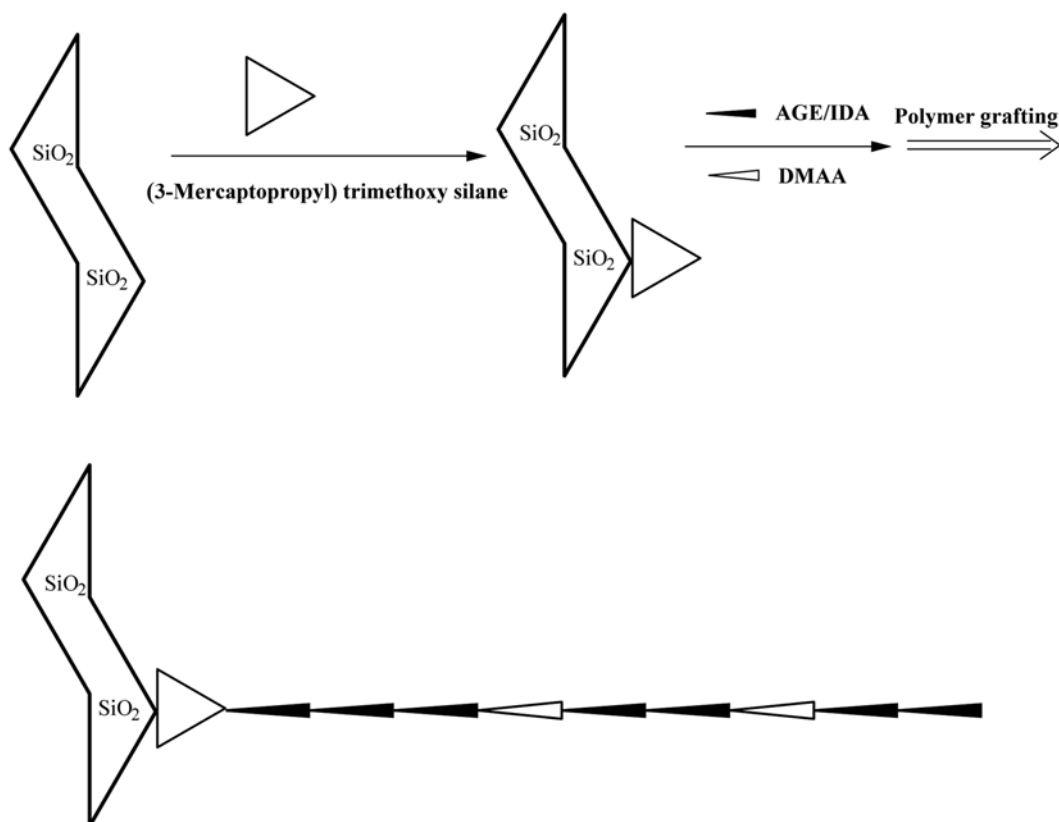


Fig. 1. Schematic presentation of synthesis and grafting process of poly(AGE/IDA-co-DMAA)-grafted silica gel.

co-DMAA)-grafted silica gel was added. The solution of poly(AGE/IDA-co-DMAA)-grafted silica gel mixtures was stirred at 120 rpm at optimum pH range and ambient temperatures, using a shaker. The difference between the initial and the final value gives the amount of Co adsorbed per gram of the adsorbent. Effect of various parameters, such as contact time and pH of the aqueous feed, was studied.

## RESULTS AND DISCUSSION

### 1. Effect of pH

The degree metal sorption at different pH values was determined by batch equilibration technique. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Co(II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from poly(AGE/IDA-co-DMAA)-grafted silica gel with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig. 2. The maximum recovery was 99.3% at pH 5.

### 2. Sorption Capacity

The 0.05 g of poly(AGE/IDA-co-DMAA)-grafted silica gel was stirred for 4 h. with 50 mL solution containing 10-100 µg·mL$^{-1}$ of Co(II) at optimum pH and 20 °C. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the sorbent for the metal ion was determined from the difference between the metal ion concentration in solution before and after the sorption. The saturated adsorption capacity of the sorbent is shown in Fig. 3. This figure indicates the effect of initial concentration of the Co(II) in the solution on sorption capacity of Co(II) by DMAA-AGE/IDA- grafted silica gel. The capacity goes up with increasing initial concentration of the Co(II) in the solution (72 mg·g$^{-1}$).
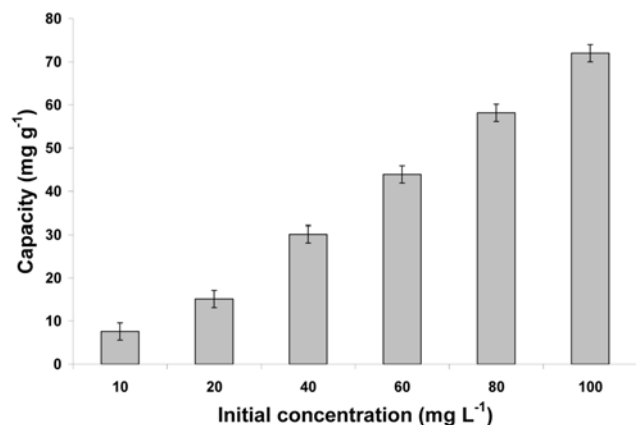
### 3. Reusability of the Sorbent

The Co(II) was sorbed and desorbed on 1 g of the poly(AGE/IDA-co-DMAA)-grafted silica gel several times. It was found that the sorption capacity of sorbent after 15 cycles of its equilibration with Co(II) changes less than 10%. Therefore, repeated use of the sorbent is feasible. The sorbent after loading with samples can be readily regenerated with 0.5 M HNO$_3$. The sorption capacity of the sorbent stored for more than 6 months under ambient conditions has been found to be practically unchanged.

### 4. Cobalt Sorption Kinetics

Poly(AGE/IDA-co-DMAA)-grafted silica gel (0.05 g) was shaken with 50 mL of solution containing 80 µg·mL$^{-1}$ of Co(II) for different periods of time (5, 15, 30, 45, 60, 90, 120 and 240 min) under optimum pH. After filtration of the sorbent, the concentration of Co(II) in solution was determined using FAAS. The sorption as a function of contact time for all the metal ions is presented in Fig. 4. Less than 5 min incubation was required for 97% sorption. The profile of Co(II) uptake reflects good accessibility of the chelating sites in the poly(AGE/IDA-co-DMAA)-grafted silica gel.

### 5. Isotherm Studies

The equilibrium data were correlated by Langmuir, Freundlich, Temkin and Redlich-Peterson equations for cobalt adsorption on poly(AGE/IDA-co-DMAA)-grafted surface. Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, with a constant energy of adsorption and no transmigration of adsorbate in the plane of the surface. The isotherm plotted in Fig. 5 is well described by the linear form of the Langmuir equation [19]:

$$C_e/q_e = (1/q_{max}\cdot K_L) + (C_e/q_{max}) \tag{1}$$

where $C_e$ (mg·L$^{-1}$) is equilibrium concentrations of Co(II), $q_e$ (mg·g$^{-1}$) is amount of Co(II) at equilibrium on poly(AGE/IDA-co-DMAA)-
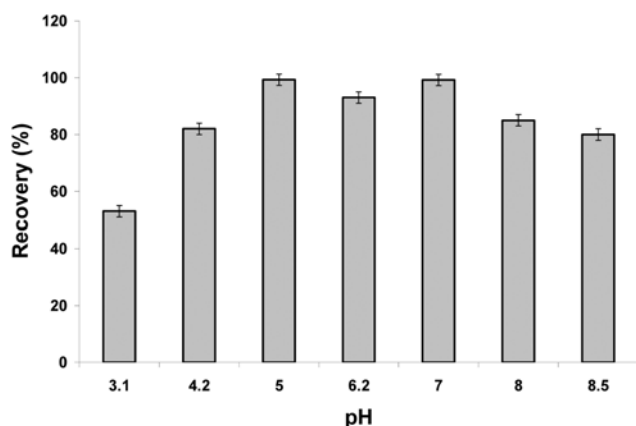


**Fig. 2. Effect of pH sorption of Co(II) onto poly(AGE/IDA-co-DMAA)-grafted silica gel.**



**Fig. 3. Effect of initial concentration of the Co(II) in the solution on sorption capacity.**
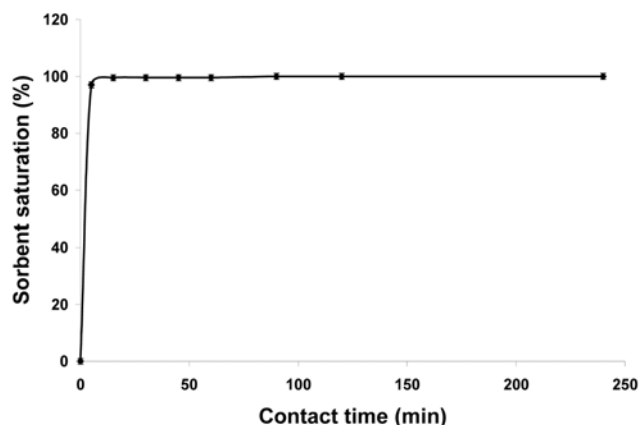


**Fig. 4. Kinetics of Co(II) sorption on poly(AGE/IDA-co-DMAA)-grafted silica gel.**
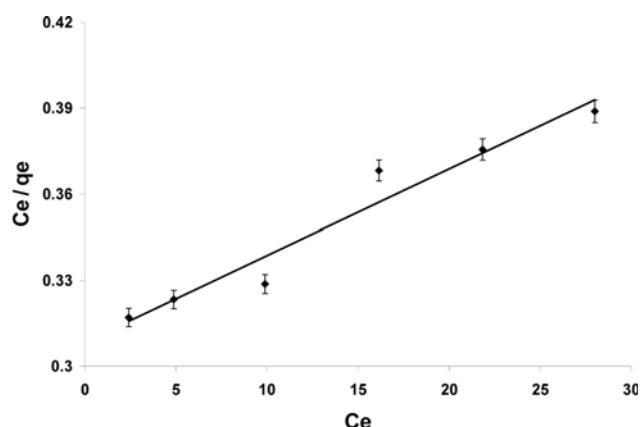
**Fig. 5. Langmuir isotherm for Co(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at 20 ℃.**

**Table 1. Isotherm parameters obtained by using linear method**

| Langmuir isotherm model | | | |
|---|---|---|---|
| Temperature (℃) | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R_L$ | $R^2$ |
| 20 | 333.3 | 0.0097 | 0.508 | 0.9510 |

| Freundlich isotherm model | | |
|---|---|---|
| Temperature (℃) | $K_F$ (mg/g) $(L/mg)^{1/n}$ | n | $R^2$ |
| 20 | 3.52 | 1.10 | 0.9987 |

| Temkin isotherm model | | | |
|---|---|---|---|
| Temperature (℃) | A (L/g) | B (J/mol) | b (J/mol) | $R^2$ |
| 20 | 0.292 | 31.651 | 77.00 | 0.9579 |

| Redlich-Peterson isotherm model | | |
|---|---|---|
| g | B $(dm^3/mg)^g$ | A $(dm^3/g)$ | $R^2$ |
| 1.1 | 0.005 | 3.2 | 0.9826 |

grafted silica gel, $q_{max}$ is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg·g⁻¹) and $K_L$ is the Langmuir constant (L·mg⁻¹) related to adsorption capacity and energy of adsorption, respectively. The data fitted well in the Langmuir equation as shown by the regression coefficient values (Table 1). The $K_L$ and $q_{max}$ values determined from the slopes and intercepts of the straight-line plot are given in Fig. 5.

Confirmation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of poly(AGE/IDA-co-DMAA)-grafted surface. The essential characteristics of a Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor, $R_L$, given by the following equation [20]:

$$R_L = 1/(1+K_L \cdot C_0) \tag{2}$$

where $C_0$ is the initial metal concentration (mg·L⁻¹) and $K_L$ is the energy of interaction at the surface. For a favorable adsorption, the separation factor $R_L$ lies between 0 and 1.

Thus, $R_L$ value of 0.508 calculated at optimum pH lies between 0 and 1.0, indicating a highly favorable adsorption (Table 1).

The Freundlich adsorption was also applied for the adsorption of cobalt by poly(AGE/IDA-co-DMAA)-grafted and is given as follows:
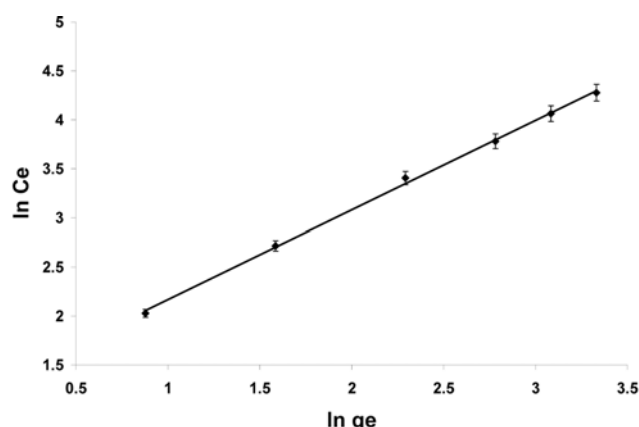


**Fig. 6. Freundlich isotherm for Co(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted gel at 20 ℃.**

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{3}$$

where $q_e$ is the amount of Co(II) adsorbed per unit weight of the adsorbent (mg·g⁻¹), $C_e$ the equilibrium concentration (mg·L⁻¹), $K_F$ the Freundlich constant (mg·g⁻¹) (L·mg⁻¹)$^{1/n}$ and 1/n is the heterogeneity factor. Linear plots of $\ln C_e$ and $\ln q_e$ show that the adsorption of cobalt on poly(AGE/IDA-co-DMAA)-grafted follows the Freundlich model (Fig. 6). The value if 1/n between 0.1 and 1 (0.91) represents good adsorption of cobalt on poly(AGE/IDA-co-DMAA)-grafted. The Freundlich equation predicts that the Co(II) concentration on the adsorbent will increase as long as there is an increase in the Co(II) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form [21]:

$$q_e = \frac{RT}{b} \ln(AC_e) \tag{4}$$

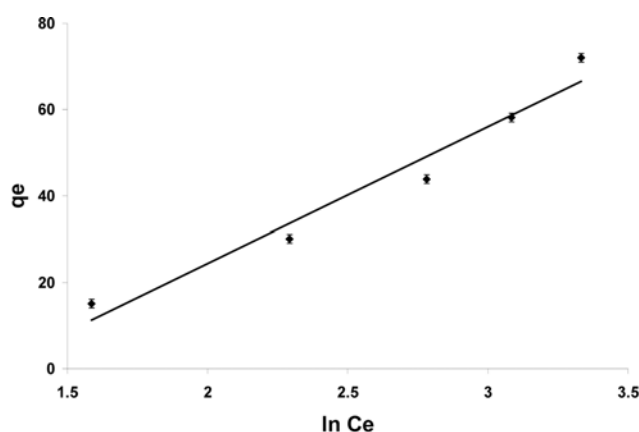and can be linearized:

$$q_e = B \ln A + B \ln C_e \tag{5}$$



**Fig. 7. Temkin isotherm for Co(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at 20 ℃.**

where B=RT/b and b is the Temkin constant related to heat of sorption (J·mol⁻¹). A is the Temkin isotherm constant (L·g⁻¹), R the gas constant (8.314 J·mol⁻¹·K⁻¹) and T is the absolute temperature (K). Therefore, plotting $q_e$ versus ln $C_e$ (Fig. 7) enables one to determine the constants A and B. Temkin parameters calculated from Eqs. (7) and (8) are listed in Table 1.

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator:

$$q_e = \frac{AC_e}{1+BC_e^g} \tag{6}$$

It has three isotherm constants, namely, A, B, and g (0<g<1), which characterize the isotherm. The limiting behavior can be summarized as follows:

Where g=1
$$q_e = \frac{AC_e}{1+BC_e} \tag{7}$$

i.e., the Langmuir form results.

Where constants A and B are much greater than unity [22]:
$$q_e = \frac{A}{BC_e^{g-1}} \tag{8}$$

i.e., the Freundlich form results.

Where g=0
$$q_e = \frac{AC_e}{1+B} \tag{9}$$

i.e., the Henry's Law form results.

Eq. (9) can be converted to a linear form by taking logarithms:

$$\ln\left(A\frac{C_e}{q_e}-1\right) = g\ln(C_e)+\ln(B) \tag{10}$$

Three isotherm constants, A, B, and g, can be evaluated from the linear plot represented by Eq. (10) by using a trial and error procedure, which is applicable to computer operation. It was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination, $R^2$, for a series of values of A for the linear regression of ln($C_e$) on ln[A($C_e$/$q_e$)−1] and to obtain the best value of A which yields a maximum 'optimized' value of $R^2$ using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

The Redlich-Peterson isotherm constants, A, B, and g as well as the coefficient of determination, $R^2$, for the sorption of Co(II) onto poly(AGE/IDA-co-DMAA)-grafted silica gel using the linear regression are shown in Table 1. It can be seen that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. The result shows that the Langmuir isotherm best fit the equilibrium data for adsorption of Co(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel.

## 6. Scatchard Analysis

Scatchard analysis, which was employed to further analyze the binding isotherms, is an approximate model commonly used in SPE characterization. The Scatchard equation can be expressed as, Q/
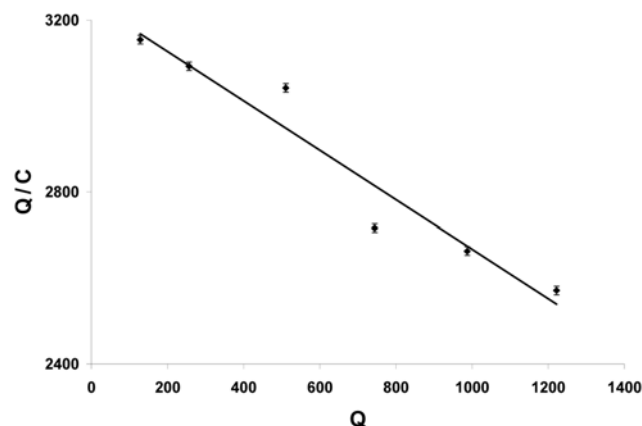


Fig. 8. Scatchard plots of Co(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at 20 ℃.

C=($Q_{max}$−Q)/$K_d$, where C (μmol·mL⁻¹) is the equilibrium concentration of cobalt; Q (μmol·g⁻¹) is the equilibrium adsorption amount at each concentration; $Q_{max}$ (μmol·g⁻¹) is the maximum adsorption amount; and $K_d$ (μmol·mL⁻¹) is the equilibrium dissociation constant at binding sites. Fig. 8 shows the Scatchard plots of the binding of cobalt to the sorbent. It is clear that the Scatchard plot for sorbent is a single straight line. The linear regression equation was Q/C=−0.5751Q+3242.2 ($R^2$=0.9375), suggesting that the homogeneous recognition sites for cobalt were formed in the SPE sorbent. From the slope (−0.5751 (1/$K_d$)) and intercept (3242.2 ($Q_{max}$/$K_d$)), $K_d$ and $Q_{max}$ for the affinity binding sites were calculated to be 1.74 μmol·mL⁻¹ and 5637.6 μmol·g⁻¹, respectively.

## 7. Effect of Foreign Ions

To evaluate the selectivity of the preconcentration system, the effect of some metal ions (20 mg·L⁻¹) on the sorption behavior of Co(II) ion (20 mg·L⁻¹) was investigated. The extraction percentage (E %) and the distribution ratio (D) (mL·g⁻¹) were calculated. Table 2 indicates the most effective ions on adsorption of Co(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel are Zn(II), Al(III), Hg(II) and Mg(II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Co(II) on the poly(AGE/

### Table 2. Effect of other ions on sorption

| Interfering ion | A | L (%) | E (%) | D |
|---|---|---|---|---|
| - | 14 | 0 | 70.0 | 2.33 |
| Ca(II) | 13.3 | 5 | 66.5 | 2.00 |
| Hg(II) | 9.17 | 34 | 45.8 | 0.85 |
| Ni(II) | 14 | 0 | 70.0 | 2.33 |
| Ba(II) | 13.3 | 5 | 66.5 | 2.00 |
| Zn(II) | 12.3 | 12 | 61.5 | 1.60 |
| Fe(II) | 13.0 | 7 | 65 | 1.86 |
| K(I) | 13.7 | 2 | 68.5 | 2.10 |
| Na(II) | 14 | 0 | 70.0 | 2.33 |
| Al(III) | 9.8 | 30 | 49 | 1.29 |
| Mg(II) | 11.3 | 19 | 56.5 | 1.30 |
| Mixed above ions | 8.05 | 42 | 40.2 | 0.67 |

A: amount of adsorbed Co (II) (mg·L⁻¹), L: loss of adsorption (%), E: extraction percentage (%) and D: distribution ratio

**Table 3. Comparison of recovery, preconcentration and capacities with some literatures**

| Preconcentration system studied | Recovery | Preconcentration factor | Resin capacity (mg g$^{-1}$) | Reference |
|---|---|---|---|---|
| Silica Gels Modified with Triphenylphosphonium | - | - | 1.47 | [23] |
| Bis(2,4,4-trimethylpentyl) mono thiophosphinic acid | - | - | 1.58 | [24] |
| Amberlite XAD-7 impregnated with Xylenol Orange | 98 | 100 | 2.6 | [25] |
| Quinalizarin anchored on Amberlite XAD-2 | 91-99 | 25 | 93 | [26] |
| Pyrogallol Immobilized Amberlite XAD-2 | 96 | 4 | 4.1 | [27] |
| 2-{[1-(3,4-ihydroxyphenyl)methylidene]amino} benzoic acid immobilized Amberlite XAD-16 | 98.2 | 167 | 13.02 | [28] |
| Pyrocatechol modified amberlite XAD-2 resin | 97 | 10 | 12.9 | [29] |
| Dithiocarbomate onto C18- Solid phase extraction Column | 98.2 | 10 | - | [30] |
| Amberlite XAD-2 functionalized with o-aminophenol | 96 | 100 | 3.29 | [31] |
| Cellulose- pyrocatechol | 98.2 | 10 | 9.43 | [32] |
| DMAA-AGE/IDA-grafted silica gel (Our sorbent) | 99.3 | 10 | 72 | - |

IDA-co-DMAA)-grafted silica gel in presence of all mentioned ions (with each ion having the concentration of 20 mg·L$^{-1}$) shows that the Co(II) can be determined quantitatively in the environmental samples.

## 8. Comparison with other Methods

Comparative information from some studies on preconcentration of Co(II) by various methods for the figure of merits is given in Table 3. The sorption capacity and recovery of the present sorbent is superior in comparison to all the matrixs shown in Table 3. The newly developed method has been successfully applied to the analysis of trace cobalt ions in natural water sample.

## 9. Determination of Co(II) in Sea Water

Poly(AGE/IDA-co-DMAA)-grafted silica gel was used to preconcentrate and determine Co(II) ions in the Persian Gulf (Boshehr, Nuclear Power Plant, Iran). The pH of water sample was adjusted to the optimum pH 5.0. Solid phase extraction with poly(AGE/IDA-co-DMAA)-grafted silica gel coupled with FAAS was applied to determination of the Co(II) in water sample. Since no Co(II) was detected in the water sample, 100 mL water sample was spiked with 0.02, 0.04 and 0.06 mg of Co(II) before being subjected to the recommended procedure. The results, shown in Table 4, demonstrate the applicability of the procedure for cobalt determination in samples with high recovery (>90%).

## 10. Determination of Co(II) in Plasma

Adsorption of Co(II) ions on the poly(AGE/IDA-co-DMAA)-grafted silica gel from human serum was also studied batchwise. Human blood was collected from thoroughly controlled voluntary blood donors. Each unit was separately controlled and found nega-

tive for HBS antigen and HIV I, II and hepatitis C antibodies. After no detection of Co(II) in the plasma, 25 mL plasma was spiked with 0.01 mg of Co(II) before being subjected to the recommended procedure. Then 25 mL volume of human plasma containing 0.4 µg· mL$^{-1}$ of Co(II) ions was treated with 0.1 g of poly(AGE/IDA-co-DMAA)-grafted silica gel at room temperature and magnetically stirred at a speed of 600 rpm. After the desired treatment periods, the sorbent was taken out and adsorbed metal ion was eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by FAAS. The experiments were performed in replicates of three. The results (Table 4) indicate the suitability of the present sorbent for the preconcentration of cobalt from plasma samples. The similarity of results obtained by mentioned methods indicates that the reliability of the Co(II) content data presented in Table 4 is reasonable.

## 11. Figure of Merit

The analytical performance of the proposed procedure can be shown for the results from FAAS measurements. The preconcentration procedure was repeated seven times with the model solutions at the optimum working conditions in 0.6 mgL$^{-1}$ Co(II) solutions. The percent relative standard deviations (%R.S.D.) and the confidence intervals at confidence level of 95% were 3.2%. The detection limit (3 s, N=5) for the examined analytes was 0.31 µg L$^{-1}$. In the current study, the limit of detection was determined as ten times the standard deviation of the absorbance with the pre-concentration step. The limit of detection value was 1.03 µg L$^{-1}$. The regression equation (after preconcentration) was $A=0.0145C_{Co}+0.0002$ ($R^2=0.9999$), and the conventional regression equation was A=0.0040

**Table 4. Results obtained for Co(II) determination in plasma and the Persian Gulf water sample of (I), (II) and (III)**

|  | Plasma | (I) | (II) | (III) |
|---|---|---|---|---|
| Found (without spiking of Co(II)) | N.D. | N.D. | N.D. | N.D. |
| Added Co(II) (µg·mL$^{-1}$) | 0.4 | 0.2 | 0.4 | 0.6 |
| Found Co(II)$^a$ [after preconcentration (µg mL$^{-1}$)] | 0.86±0.11 | 1.83±0.10 | 3.62±0.14 | 5.41±0.12 |
| Preconcentration factor | 2.5 | 10 | 10 | 10 |
| Recovery (%) | 86 | 91.7 | 90.6 | 90.2 |

a: For three determinations

$C_{Co}+0.0001$ ($R^2=0.9998$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 3.6. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

## CONCLUSION

A new method was developed for the determination of trace metals in various environmental solid/liquid samples. As a result of a 10-fold preconcentration factor, the method was found to be applicable to environmental waters, including streams, rivers, and lakes, as well as to seawater. The system was also successful in preconcentrating metal ions from biological samples. The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments, and cost-effectiveness. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of poly(AGE/IDA-co-DMAA)-grafted silica gel was as high as greater than 10 cycles without any loss in its sorption behavior. Some parameters obtained were comparable to those presented by other methods described in the literature. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 333.3 (mg·g$^{-1}$) at 20 $^{\circ}$C. The $R_L$ values showed that the poly(AGE/IDA-co-DMAA)-grafted silica gel was favorable for the adsorption of Co(II). Preconcentration by this sorbent combined with FAAS can be applied to the determination of trace Co(II) ions in human plasma and the sea water samples with satisfactory results.

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