고상에서 용액으로 부터 카드뮴 추출과 잔유물 측정

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Cadmium Extraction from Solutions by Solid-Phase and its Trace Determination

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요 약. 고상추출 매질로 bis-(2-ethylhexyl)phthalate를 포함하는 polyvinyl chloride막을 사용하여 카드뮴의 잔유양을 측정하기 위한 새로운 민감하고 선택적인 분광광도법을 연구하였다. Bis-(2-ethylhexyl)phthalate는 가소제로 사용되었다. 수용액에서 Cd(II)은 색을 가진 Cd(II) - I⁻ - MG 착체(여기서 MG는 malachite green이다). 형으로 있는 막에 의해 트랩되었고, 카드뮴 착체는 막에 농축되었다. 그린색의 막의 흡수는 분광광도법을 사용하여 629 nm에서 측정되었다. 카드뮴 농도는 Cd(II) 농도와 25분 동안 착색후 막의 흡수 사이에 관계로 나타내는 검정곡선으로부터 계산하였다. 검정곡선은 시험용액에서 10-760 μgL⁻¹ cadmium 범위에서 선형이었다. 3Sbl criterion의 검출한계는 1.8199 μgL⁻¹ 상대 표준편차(RSD)는 4% (n=5)보다 적다. 제안된 방법은 Tadjan강(Sari-Iran), 에 있는 카드뮴의 잔량을 성공적으로 측정하였다. 28.7 μgL⁻¹의 평균 값을 얻었다.

주제어: Polyvinyl chloride 막; Bis-(2-ethylhexyl)phthalate; Malachite green; 고상추출

ABSTRACT. A new sensitive and selective spectrophotometric method for determination of trace amounts of cadmium using a polyvinyl chloride membrane containing bis-(2-ethylhexyl)phthalate as a solid phase extraction medium was investigated. Bis-(2-ethylhexyl)phthalate has used as a plasticizer. Cd(II) in an aqueous solution was trapped on the membrane in the form of colorful Cd (II)-I⁻ - MG complexes (which MG is malachite green) and the cadmium complex was concentrated in the membrane. The absorbance of the green membrane was measured at 629 nm using a spectrophotometer, and then, the concentration of the cadmium was calculated using a calibration curve, which expressed the relationship between the Cd(II) concentration and the membrane absorbance after coloring for 25 min. The calibration curve was linear in the range of 10-760 μgL⁻¹ cadmium in the test solution. The detection limit based on the 3S$_{bl}$ criterion was 1.8199 μgL⁻¹ and the relative standard deviations (RSD) were less than 4 % (n=5). The proposed method has been successfully applied to the determination of trace amounts of cadmium in the Tadjan River water sample (Sari-Iran), and the mean value of 28.7 μgL⁻¹ was obtained.

Keywords: Polyvinyl chloride membrane; Bis-(2-ethylhexyl)phthalate; Malachite green; Solid-phase extraction

INTRODUCTION

Cadmium is a heavy metal that is toxic for human beings, animals and plants and is one of the most serious environmental pollutants. The International Agency for Research on Cancer (IARC) classified cadmium as a human carcinogen. Roughly 15,000 t of cadmium is produced worldwide each year for nickel-cadmium batteries, pigments, chemical stabilizers, metal coatings and alloys. Cadmium enters the organism primarily via the alimentary and respiratory tract. The sources of absorbance of this metal are foods, drinking water and air. Also a large amount of this metal is found in the wastewaters of the industrial factories.[1] Additions of cadmium into the watercourses by industrial activities are different. For example, 0.1 mgL^{-1} for the surface treatment of metal and plastics, and 0.2 mgL^{-1} for the painting and electrical industry Have used.[2] Therefore preconcentration and determination of trace cadmium from the natural water and wastewaters of the factories are very important and need much more attention. The traditional preconcentration and separation methods for Cd (II) are liquid-liquid extraction, coprecipitation and ion-exchange, etc.[3,4] These methods often require large amounts of high purity organic solvents, some of which are harmful to health and create environmental problems. Nowadays, the solid phase extraction (SPE) is being utilized for preconcentration of heavy metals and the need of more selective systems for separation of trace elements have increased the development of the synthesis of new extractants and adsorbents.[1]

In this study, a PVC film extraction method for the determination of trace amounts of Cd (II), based on Cd (II)-I⁻ -MG coloring system, was developed. The Cd (II)-I⁻ -MG complex was extracted and concentrated onto the PVC film and The absorbance of the colored membrane was measured directly by using a spectrophotometer, and the concentration of cadmium was calculated by using a calibration curve. This method offers important advantages: 1) the method is selective and free from the interferences caused by iron, zinc and copper ions in the samples. The use of PVC membrane that does not con-

tain complexing agent is useful for selecting a suitable ligand and complexing agent which possess high sensitivity to cadmium;[5] 2) the method is environmentally safe since the use of toxic extraction solvents such as isobutylmethylketone, xylene and trichlorotrifluoroethan, which are employed in liquid-liquid extractions of cadmium, are eliminated;[6] 3) the extraction method is economical because there is no need of expensive extraction solvents;[6] 4) the PVC membrane does not need further treatment after it is colored and the method is simple compared to the labor and time consuming steps such as back extraction which is usually required in liquid-liquid extractions.[7]

EXPERIMENTAL SECTION

Apparatus. Membrane absorbance was measured by a GBC UV-VIS Cintra 20 model spectrophotometer. To adjust pH and prepare the buffer solution a JENWAY model 3510 digital pH meter was used.

Materials. All reagents were of analytical grade. Deionized water was used throughout.

Sample analysis was performed using the following chemical reagents: Bis-(2-ethylhexyl)phthalate (Merck, Germany); PVC powder(Vestolit, Germany), which consists of the K-value of 67; $NaCH_3COO/CH_3COOH$ buffer solution (pH 4), which was prepared from mixing 4.7927 mL acetic acid (Merck, Germany) and 1.2633 g sodium acetate (Merck, Germany) in deionized water and diluting to the mark in a 100 mL volumetric flask; KI solution (0.9%), which was prepared by dissolving 0.9 g KI (Merck, Germany) in 99.1 g deionized water, note that 5 drops of 0.1 M $Na_2S_2O_3$ (Merck, Germany) must be added to the KI solution to avoid changes in I⁻ oxidation number; malachite green oxalate (MG) solution (0.06%), which was prepared by dissolving 0.06 g malachite green oxalate(sdFine, India) in 99.94 g deionized water; Cd (II) 100 mgL^{-1}, which was prepared by dissolving 0.2305 g $3CdSO_4.8H_2O$(Merck, Germany) in a small amount of deionized water and diluting it to 1000 mL in a volumetric flask. This solution was diluted to the desired

concentration when used.

Preparation of PVC membranes. 45 g bis-(2-ethylhexyl)phthalate as a plasticizer and 55 g PVC powder were placed into a beaker and was stirred with a paddle agitator. At first the paste was hard and after high-speed stirring the mixture formed a smooth paste. A small amount of the prepared paste was expanded on a flat glass surface and was heated in a 140 °C oven for 40 seconds. The membrane produced in this way was cut into 1×2 cm pieces, and was then ready for use.

Measurement procedure. 10 mL of aqueous sample solution containing Cd (II) and 2 mL of KI solution were placed into a glass beaker. Drops of acetic acid 1% were added to achieve pH=4. To adjust pH, 2 mL of $NaCH_3COO/CH_3COOH$ buffer solution (pH=4) was added. Then 1 mL malachite green oxalate solution was added into the beaker and the mixture was diluted to the mark in a 25 mL volumetric flask with deionized water. A sheet of PVC membrane was immersed into the solution and the mixture was stirred for 25 minutes in water bath at 50 °C. The resulting colored film was rinsed with deionized water and wiped to remove any water droplets. The same procedure was applied for standard Cd (II) solutions (25-2500 μgL⁻¹), in order to make colored membranes. The absorbance of the colored membranes was measured 5 times at 629 nm against reagent blank film using a visible spec-

trophotometer. Results of the measurements and the calculated amounts of standard deviation (SD), average and relative standard deviation (RSD) are shown in *Table* 1. The concentration of Cd (II) was calculated from the calibration curve.

RESULTS AND DISCUSSION

Coloring mechanism of PVC membrane. The PVC membrane that does not contain complexing agent acts as a carrier for adsorption, extraction and concentration of the colorful complexes.[3] The mechanism of formation of colorful complexes is as following:

$$Cd(II) - 4I^- \rightarrow CdI_4^{2-} \qquad k_f = 2/5 \times 10^6$$
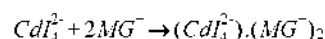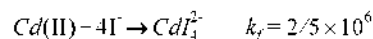
$$CdI_4^{2-} + 2MG^- \rightarrow (CdI_4^{2-}).(MG^-)_2$$

According to this mechanism Cd (II) combines with I into CdI_4^{2-} metal complex anion. Then MG which exists in aqueous solution in the form of cationic malachite green (MG^+), associates with CdI_4^{2-} to form $(CdI_4^{2-}).(MG^-)_2$ ion-associated complex. This colorful ion-associated complex is extracted on PVC membrane by surface adsorption and the colored membrane is formed as a result.

Effect of KI concentration on the absorbance of the membrane. Keeping other variables con-

Table 1. Results of the measurements and the calculated amounts of SD, average and RSD

| C(μg/L) \ Signal	s1	s2	s3	s4	s5	SD	Average	RSD%
10	0.0156	0.0149	0.0151	0.0150	0.0160	0.000465833	0.0153	3.0418
40	0.0311	0.0309	0.0318	0.0321	0.0316	0.000494975	0.0315	1.5714
120	0.0613	0.0622	0.0625	0.0623	0.0629	0.000589915	0.0622	0.9479
200	0.0982	0.0974	0.0988	0.0975	0.0971	0.000689202	0.0978	0.7045
280	0.1479	0.1487	0.1480	0.1485	0.1493	0.000567450	0.1485	0.3819
360	0.1862	0.1863	0.1857	0.1872	0.1854	0.000687750	0.1862	0.3696
440	0.2201	0.2211	0.2196	0.2205	0.2212	0.000674537	0.2205	0.3061
520	0.2589	0.2596	0.2603	0.2598	0.2607	0.000687750	0.2599	0.2647
600	0.3052	0.3047	0.3066	0.3048	0.3063	0.000875785	0.3055	0.2867
680	0.3496	0.3488	0.3503	0.3485	0.3492	0.000704982	0.3493	0.2018
760	0.3766	0.3777	0.3768	0.3772	0.3761	0.000605805	0.3769	0.1608
840	0.4399	0.4417	0.4411	0.4403	0.4414	0.000756307	0.4409	0.1715
920	0.4798	0.4806	0.4805	0.4789	0.4799	0.000680441	0.4799	0.1417
1000	0.4942	0.4953	0.4957	0.4948	0.4951	0.000563028	0.4950	0.1137
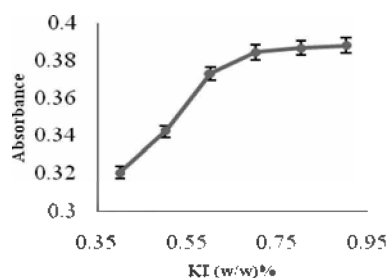
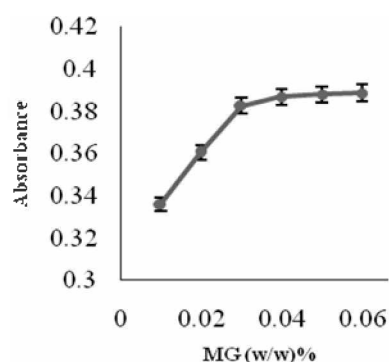*Fig.* 1. Effect of KI concentration on the absorbance of the membrane.

Fig. 2. Effect of MG concentration on the absorbance of the membrane.

stant and varying KI concentration, we studied the effect of KI concentration on the absorbance of the membrane. The absorbance was improved regularly with increasing the concentration of KI. When the concentration increased to 0.8%, the absorbance reached to a constant value (*Fig.* 1), and did not change with further increase in KI concentration. Thus 0.9% KI was selected to ensure that Cd (II) has completely formed CdI_4^{2-} metal complex anion.

Effect of MG concentration on the absorbance of the membrane. The effect of MG concentration on the absorbance of the membrane was studied. *Fig.* 2 shows that an increase in the absorbance was observed with an increase in MG concentration until 0.05%. Furthermore, the absorbance of the membrane did not change with further increase in MG concentration, which means that the whole Cd (II) in the solution has formed $(CdI_4^{2-}).(MG^-)_2$ ion-associated complexe. Hence, the use of 0.06% MG was recommended as an optimum concentration.
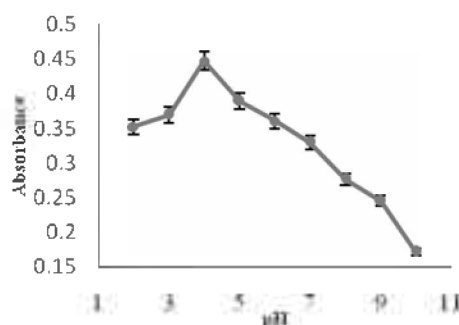

Fig. 3. Effect of pH on the absorbance film of the membrane. on the absorbance.

Effect of pH on the absorbance of the membrane. A study of the relationship between the absorbance of the colored membrane and pH was conducted. The results showed that the most suitable pH is 4 (*Fig.* 3). It seems that it is the most appropriate pH for the Cd (II) to combine with I⁻ into metal complex anion. Note that the pH should not rise above 7 because cadmium hydroxide precipitates at high pH values and less ion-associated complex is formed and consequently a decrease in the extraction of Cd (II) will occur.

Effect of plasticizer content of the PVC film on the absorbance of the membrane. PVC films with different plasticizer contents were made and the effect of plasticizer content of the film on the extraction of the colorful cadmium complex was studied. The absorbance of the colored membranes was measured at 629 nm by a visible spectrophotometer (*Fig.* 4). Although the extraction rate of
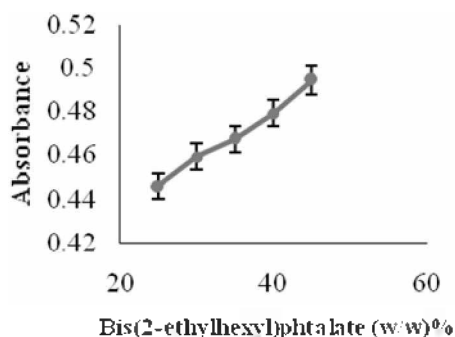

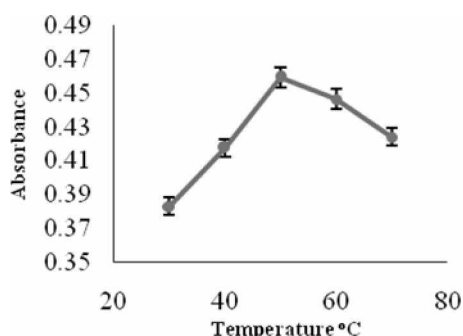*Fig.* 4. Effect of plasticizer content of the film of the membrane.

Fig. 5. Effect of temperature of water bath on the absorbance of the membrane.

colorful complex increases with increase of plasticizer content, the films become softer because they contain more plasticizer and thus are difficult to handle. The most effective film is one which contains about 45% plasticizer.

Effect of temperature and stirring time on the absorbance of the membrane. The effect of temperature and stirring time were also investigated. The experiments showed that the most suitable temperature of the water bath was 50 °C and in higher temperatures a decrease in the absorbance of the membrane was observed (Fig. 5). It is likely that complex decomposes in temperatures above 50 °C.

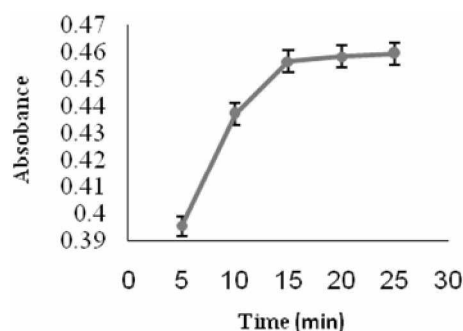The study of the stirring time showed a distinct

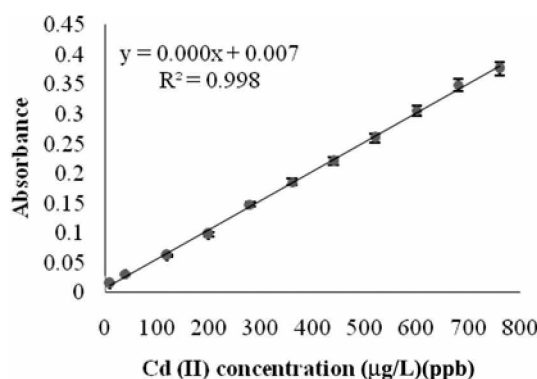Fig. 6. Effect of stirring time on the absorbance of the membrane

Fig. 7. Representative calibration graph of cadmium ion concentration.

improvement in the absorbance with increase in stirring time (Fig. 6). Over 20 minutes the absorbance reached to a constant value and did not change with prolongation of stirring time. Therefore 25 minutes was selected as the best reaction time.

Calibration curve. Fig. 7 shows the calibration curve of absorbance at 629 nm (due to the (CdI_4^{2-}). $(MG^+)_2$ complex) as a function of Cd (II) concentration. The curve is linear over the Cd (II) concentration of 10-760 μgL^{-1} and is expressed by the linear equation: $A=0.0005C+0.0073$, where A is the absorbance of the membrane and C is the concentration of Cd (II) in μgL^{-1} in the colorful test solution. The linear correlation coefficient, γ, is 0.9986.

In order to calculate the detection limit, the absorbance of the reagent blank film was measured 5 times at 629 nm using a visible spectrophotometer (Table 2) and the detection limit of 1.8199 μgL^{-1} was obtained according to the equation1.

Table 3. Measured absorbances in presence of interfering ions and relative standard errors

	in presence of Zn(II)	in presence of Cu(II)	in presence of Fe(III)
Signal	0.1003	0.1025	0.0999
E. (%)	2.5562	4.8361	2.1847

Table 2. Measurement data for calculating the detection limit

Signal	S1	S2	S3	S4	S5	SD
Blank	0.0018	0.0021	0.0017	0.0015	0.0013	0.000303315

Table 4. Determination of cadmium ion concentration in the Tadjan river water sample (Sari- Iran)

	S2	S3	S4	S5	average	RSD (%)
Absorbance of the membrane	0.0134	0.0130	0.0128	0.0131	0.0129	0.0130	1.7709
Cd (II) concentration in the colorful test solution (µg/L)	12.2000	11.4000	11.0000	11.6000	11.2000	11.4800	4.0107

$$DL = (3S_{bl}) / m \qquad (1)$$

Effect of foreign ions. The effect of foreign ions was studied with the intention of applying this method to determine the concentration of trace amounts of Cd (II) in samples. 10 mL of 500 µgL^{-1} Cd (II) solution has put into a 25 mL volumetric flask and 2.5 mL of interfering ion with the concentration of 10^6 µgL^{-1} was added and the procedure was done (final volume is 25 mL) and the absorbance of the membrane was measured at 629 nm. The relative measurement error was calculated according to equation 2, where x_i is the absorbance of the membrane in presence of Cd (II) without any interfering ion and is equal to 0.0978 according to the measurements. As it is shown in *Table* 3, the relative measurement error is less than 5% even in presence of high concentrations of foreign ions.

$$E_r(\%) = [(x_i - x_j)/x_i] \times 100 \qquad (2)$$

Applications. The proposed method has been applied successfully to the determination of Cd (II) concentration in the Tadjan River's water (Sari-Iran). 10 mL of river water was poured into a glass beaker and 2 mL KI solution was added. In addition, acetic acid 1% was added drop wise to achieve pH = 4 and then the pH were adjusted at 4 by adding 2 mL buffer solution. 1 mL malachite green oxalate solution was added into the beaker and the mixture was diluted with deionized water to the mark in a 25 ml volumetric flask. A sheet of PVC membrane was placed into this colorful test solution and the mixture was stirred for 25 min in water bath at 50 °C. The colored membrane was rinsed with deionized water and wiped. The absorbance of the membrane was measured 5 times using the spectrophotometer at 629 nm. The results of the analysis are shown in *Table* 4.

The concentration of Cd (II) in the colorful test solution is 11.48 µgL^{-1} according to the calibration curve. Note that 10 mL of the river water sample was used and the total volume of the colorful test solution was 25 mL after adding KI, buffer, MG solutions and deionized water. Thus the concentration of Cd (II) in the river water sample is 28.7 µgL^{-1} according to equation 3, where V_1 is the total volume of the colorful test solution (25 ml); C_1 is the Cd (II) concentration in the colorful test solution (11.48 µgL^{-1}); V_x is the volume of the river water sample (10 mL) and C_x is the concentration of Cd (II) in the river water sample.

$$C_x. V_x = C_1. V_1 \qquad (3)$$

CONCLUSION

A polymeric PVC membrane has been used as the solid phase adsorbent for extraction and determination of trace amounts of Cd (II) in aqueous solutions. The preparation of the solid adsorbent is very simple and the colored PVC membrane can be kept for a few weeks without any change in the extracted species. The procedure has the advantage of avoiding organic solvents during the extraction step. No preconcentration and elution step is required and the experimental procedure is easy to carry out. Simplicity, high speed and freedom from interference have made this method suitable for the determination of cadmium in river water samples.

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