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Study on the Solid Phase Extraction and Spectrophotometric Determination of Cadmium

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In this paper, a new chromogenic reagent, 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine (HNSR) was synthesized. A high sensitive, selective and rapid method for the determination of cadmium based on the rapid reaction of cadmium with 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine and the solid phase extraction of the coloured chelate with a MCI-GEL reversed phase polymer resin has been developed. In the presence of 0.05-0.5 mol L^{-1} of hydrochloric acid solution and emulsifier-OP medium, 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine reacts with cadmium to form a red chelate of a molar ratio 1:2 (cadmium to 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine). This chelate was enriched by the solid phase extraction with a cartridge packed with MCI-GEL polymer resin and eluted the chelate from cartridge with dimethyl formamide (DMF). The enrichment factor of 100 was achieved. In the DMF medium, the molar absorptivity of the chelate is 1.54×10^5 L mol^{-1} cm^{-1} at 505 nm. Beer's law obeyed in the range of 0.01~2.0 μg mL^{-1} in measured solution. The relative standard deviation for eleven replicates sample of 0.5 μg L^{-1} level is 2.64 %. The detection limit, based on the three times of standard deviation is 0.01 μg L^{-1} in original sample. This method was applied to the determination of cadmium in tobacco and water sample with good results.

Keywords: Cadmium, Spectrophotometry, MCI-GEL polymer resin, 5-(2-Hydroxy-4-nitrophenylazo)thiorhodanine.

INTRODUCTION

Cadmium is a highly toxic element which has been described as one of the most dangerous elements in the biological system and environment[1,2]. The Chinese Standards for Environment requires that the concentration of cadmium should not be exceeded 0.01 mg L^{-1} in water and 0.1 mg kg^{-1} in food.[3] Therefore, the determination of traces cadmium in biological and environmental samples is very important. Although several sophisticated techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), electrochemical, spectrofluorimetry, neutron activation analysis and the like have widely been applied to the determination of cadmium[4-6]. But the spectrophotometric method still has the advantages for which is simple and do not need expensive or complicated test equipment. For this reasons, a wide variety of spectrophotometric methods for the determination of cadmium have been reported, each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity[7-11]. However, the routine spectrophotometric methods are often not sensitive enough to determine low concentration of cadmium ion in biological samples, the cadmium concentration only mg kg^{-1} or μg L^{-1} level. For the determination low concentration of cadmium ion, a preconcentration step is usually required.

Solid phase extraction is an attractive technique because of it notable advantages. In our previous works, the determination of some trace metal ions by solid phase extraction with reserved phase silica-bond with C_{18} cartridge was studied[12,13]. However, the routine reserved phase silica-bond C_{18} cartridge only can use in pH range of 2~8. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, in this paper, the colour reaction of 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine (HNSR) with cadmium and the solid phase extraction of Cd-HNSR chelate with a reversed phase MCI-GEL polymer resin was study. The MCI-GEL is a reversed-phase polymer provides a broad range of solvent choices and a pH range from 0~14 and it had been used for the solid phase extraction of metal ions in various acid medium[14-16]. By using the cartridge packed with MCI-GEL polymer resin, the Cd-HNSR chelate was enriched by solid phase extraction in hydrochloric acid medium and the enrichment fact of 100 was achieved. Base on this, a highly sensitive, selective and rapid method for the determination of cadmium in tobacco and water samples was developed.

EXPERIMENTAL

A UV-2401A spectrophotometer (Shimidzu Corporation, Tokyo, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ-200 pH meter (Beckman Instruments, Fullerton, CA, USA). The extraction was performed on Waters Solid Phase Extraction (SPE) device (It can prepare twenty samples simultaneously) and a reversed phase cartridge packed with MCI GEL polymer resin (Beijing Genosys Technologies, P.R. China) was used.

MCI GEL CHP 20Y was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). MCI GEL CHP 20Y is an aromatic type adsorbent in the standard grade and is based on cross-linked polystyrenic matrix. Its particle size is 30 μm and surface area is 560 m^2 g^{-1}. It is a reversed-phase resin widely used in different industrial fields.

Synthesis of 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine: In a 100 mL beaker, a 1.54 g of 4-nitro-2-aminophenol was dissolved in 45 mL of 95 % alcohol. To this solution, 12 mL of 6 mol L^{-1} HCl were add and then cool the solution to 0 °C. After this, 7 mL of 10 % $NaNO_2$ was added slowly with stiring to obtain a diazotized salt. In another 200 mL beaker, 1.48 g of thiorhodanine and 14 mL of 7.5 mol L^{-1} ammonia were added. After the solution has been cooled to 0 °C, the above diazotized solution was added dropwise and left the mixture overnight. The solution is then acidified to pH 1 with concentrated HCl and the precipitate was isolated by filter. The crude product was recrystallized with 90 % ethanol for 3 times and the pure HNSR was obtained with a 62 % yield. Its structure was be verified by IR, ^{1}H NMR, MS spectrometry and elemental analysis. Elemental analysis: $C_9H_6N_4O_3S_3$, calculated (found), 34.39 (33.98) % C, 1.92 (2.03) % H, 17.82 (17.64) % N, 30.60 (30.28) % S. IR (KBr, cm^{-1}): 3600 ν(-OH), 3280 ν(-N-H); 3080, 3050 ν(C=C-H); 1565, 1360 ν(-N=O); 1660 δ(N-H); 1548, 1515, 1450 ν(C=C); 1292 ν(C-N); 1171, 1215 ν(C=S); 825 δ(Ar-H); 806 δ(C=C-H). ^{1}HNMR (solvent: acetone-d_6) (δ, ppm): 4.85 (1H, s, O-H, H 1); 7.68 (1 H, s, Ar-H, H 2); 7.78 (1 H, d, Ar-H, H 3); 7.25 (1 H, d, Ar-H, H 4); 2.56 (1H, s, -C-H, s, H 5). MS (EI) (*m/z*): 314 (M^{+}). All those show that the HNSR has the structure in Fig. 1.

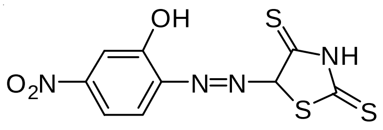

Fig. 1. Structure of HNSR

All solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). HPLC grade dimethyl formamide (DMF) (Fisher Corporation, USA) was used. A 3.0 × 10^{-4} mol L^{-1} of HNSR solution was prepared by dissolving HNSR in DMF. A stock standard solution of cadmium (1.0 mg mL^{-1}) was obtained from Chinese Material Standard Center and a work solution of 0.5 μg mL^{-1} was prepared by diluting this solution. A 2.0 mol L^{-1} of hydrochloric acid was used. Emulsifier-OP solution (2.0 % (v/v)) was prepared by dissolving emulsifier-OP with water. All chemical used were of analytical grade unless otherwise stated.

General procedure: To a standard or sample solution containing no more than 2 μg of Cd(II) in a 100 mL of calibrated flask, 5 mL of 2 mol L^{-1} of hydrochloric acid solution, 5 mL of 3.0 × 10^{-4} mol L^{-1} HNSR solution and 3 mL of 2.0 % emulsifier-OP solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 10 min, the solution was passed through the cartridge at a flow rate of 20 mL min^{-1}. After the enrichment was finished, the retained chelate is eluted from the cartridge at a flow rate of 5 mL min^{-1} with 1 mL of DMF in the reverse direction. The eluent was adjusted to the accurate volume of 1 mL in a 1 mL calibrated flask by adding microamount of DMF with a 200 μL syringes. The absorbance of this solution was measured at 505 nm in a 1 cm microcells (0.5 mL) against a reagent blank prepared in a similar way without cadmium.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of HNSR and its Cd(II) chelate are shown in Fig. 2. The absorption peaks of HNSR and its Cd complex in DMF medium are located at 405 and 505 nm.

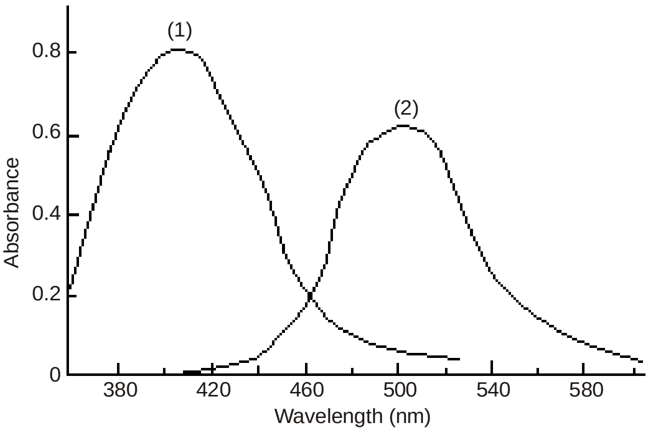

Fig. 2. Absorption spectra of HNSR and its Cd(II) complex: (1) HNSR-emulsifier-OP blank against water; (2) HNSR-emulsifier-OP-Cd(II) chelate against blank reagent blank

Effect of acidity: Results showed that the optimal condition for the reaction of Cd(II) with HNSR is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid, *etc.*, on the colour reaction of Cd(II) with HNSR was studied. The results shows that hydrochloric acid has the best effects and the concentration of hydrochloric acid within a 0.02-0.5 mol L^{-1} was found to give a maximum and constant absorbance, so 2.0 mL of hydrochloric acid was recommended.

Effect of surfactants: The effects of surfactants on Cd(II)-HNSR system were studied. The results (Table-1) showed that in the absence of surfactants, anionic surfactants or cationic surfactants, the Cd(II)-HNSR chromogenic system give a low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly. Various of nonionic surfactants enhance the absorbance in the following sequence: Emulsifier-OP > Tween-80 > Tween-20 > Tween-60. Accordingly, the emulsifier-OP was the best additive and the use of 1.5~4 mL of emulsifier-OP solution give a constant and maximum absorbance. Consequently, the use of 3 mL was recommended.

Effect of 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine concentration: For up to 2 μg of Cd(II), the use of 5 mL of

TABLE-1
EFFECT OF SURFACTANTS ON Cd(II)-HNSR CHROMOGENIC SYSTEM

Surfactant	Absence	Emulsifier-OP	Tween-80	Tween-20	Tween-60	SDS	CTMAB	CPB
λ_{max} (nm)	485	505	495	488	500	485	490	485
ε ($\times 10^4$) L mol^{-1} cm^{-1}	8.64	15.4	12.4	13.2	12.8	7.68	8.21	8.07

3.0×10^{-4} mol L^{-1} of HNSR solution was found to be sufficient for a complete reaction. Accordingly, 5.0 mL of HNSR solution were added in all further measurement.

Stability of chromogenic system: After mixing the components, the absorbance reaches its maximum within 5 min at room temperature and remains stable for at least 4 h. After having been extracted into the DMF medium, the chelate was stable for at least 8 h.

Solid phase extraction: In this study, HNSR can reacts with Cd(II) and form stable chelates in acid medium. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, a reversed phase cartridge packed with MCI-GEL polymer with pH range 0-14 was selected. MCI GEL CHP 20Y is an aromatic type adsorbent in the standard grade and is based on cross-linked polystyrenic matrix. It is a reversed-phase solid phase cartridge provides a broad range of solvent choices and a pH range from 0~14.

Both the enrichment and the elution were carried out on a Waters SPE device (which can prepare twenty samples simultaneously). The flow rate was set to 20 mL min^{-1} when enrichment and 5 mL min^{-1} when elution. Some experiments were carried out in order to investigate the retention of HNSR and its Cd(II) chelate on the cartridge. It was found that the HNSR and its Cd(II) chelate was retained on the cartridge quantitatively when they pass the cartridge as hydrochloric acid medium. The capacity of the cartridge was determined as 22 mg for Cd(II)-HNSR chelate in a 100 mL of solution. In this experiment, the maximum amount cadmium is only 2.0 μg. Therefore, the cartridge has adequate capacity to enrich the Cd(II)-HNSR chelate.

In order to choose a proper eluant for the retained HNSR and its Cd(II) chelate, various organic solvents were studied. For eluting the Cd(II)-HNSR chelates from the cartridge, the volume of the solvent needed is 0.9 mL for DMF, 1.1 mL for isopentyl alcohol, 1.3 mL for acetone, 1.4 mL for acetonitrile, 1.6 mL for ethanol, 1.8 mL for methanol. The maximal enrichment was achieved when DMF was selected as eluant. So the DMF was selected as eluant. The experiment shows that it was easier to elute the retained HNSR and its Cd(II) chelate in reverse direction than in forward direction, so it is necessary to upturned cartridge when elution. 1 mL of DMF was sufficient to elute the HNSR and its Cd(II) chelate from cartridge at a flow rate of 5 mL min^{-1}. The volume of 1 mL was selected.

Calibration curve and sensitivity: The calibration curve showed that Beer's law is obeyed in the concentration range of 0.01~2.0 μg Cd(II) per mL in the measured solution. The linear regression equation obtained was $A = 0.771\ C$ (μg mL^{-1}) + 0.0156 ($r = 0.9995$). The molar absorptivity was calculated to be 1.54×10^5 L mol^{-1} cm^{-1} at 405 nm. The relative standard deviation at a concentration level of 0.5 μg L^{-1} of Cd(II) (11 repeats determination) was 2.64 %. The detection limit, based on the three times of standard deviation is 0.01 μg L^{-1} in the original sample.

Interference: The selectivity of the proposed method was investigated by the determination 0.5 μg 100 mL^{-1} of Cd(II) in the presence of various ions within a relative error of ± 5 % are given in Table-2. The result shows that most common ions do not interfere with the determination. This method is highly selective.

TABLE-2
TOLERANCE LIMITS FOR THE DETERMINATION OF
0.5 μg OF Cd(II) WITH HNSR (RELATIVE ERROR ± 5 %)

Ion added	Tolerate (mg)
NO_3^-, K^+, BO_3^{3-}, Na^+	20
Li^+, Al^{3+}, PO_4^{3-}, NO_2^-, SO_4^{2-}, ClO_4^-, PO_4^{3-}	10
Ca^{2+}, Mg^{2+}, SO_3^{2-}, Sr^{2+}, Ba^{2+}, IO_3^-, BrO_3^-, ClO_3^-	5
Mn^{2+}, Ce^{4+}, W^{6+}, Mo^{6+}, U^{4+}, Fe^{3+}	2
Ti^{4+}, Bi^{3+}, V^{5+}, Cr^{6+}, Zr^{4+}, F^-, Fe^{2+}	1
Au^{3+}, Cr^{3+}, La^{3+}, Sn^{4+}, Zn^{2+}, Zr^{4+}, Co^{2+}, Ni^{2+}	0.5
Ru^{3+}, Bi^{3+}, Pb^{2+}, Sb^{3+}, Th^{4+}, Br^-, Os^{8+}, I^-, Cu^{2+}	0.2
Se^{4+}, Te^{4+}, $S_2O_3^{2-}$, Ag^+	0.05
Ir^{4+}, Rh^{3+}, Ru^{3+}	0.02
Pt^{4+}, Pd^{2+}, Hg^{2+}	0.01

Composition of the complex: The composition of the complex was determined by continuous variation and molar ratio method. Both showed that the molar ratio of Cd(II) to HNSR is 1:2.

Applied to the samples: For tobacco samples, 0.25 g of sample was weighted accurately into the 25 mL Teflon high-pressure microwave acid-digestion bomb. To which, 3 mL of concentrated nitric acid and 3 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 6 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 5 mol L^{-1} of hydrochloric acid solution and the preconcentration procedure given above was applied to the samples. The results were shown in Table-3.

For water samples, the samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples. The results were shown in Table-4.

Conclusion

A comparison of the possibilities of the HNSR with those of other methods for the determination of cadmium was given in Table-5. In this work, a highly sensitive and selective reagent for cadmium was synthesized. Experiment shows that HNSR can react with cadmium rapidly at room temperature in hydrochloric acid medium and most of the foreign ions do not interfere with the determination. This reagent is high selectivity. The molar absorptivity of the chelate reaches 1.54×10^5 L

TABLE-3
DETERMINATION RESULTS OF CERTIFIED STANDARD BIOLOGICAL SAMPLES

Samples	Standard value (μg/g)	By this method (μg/g)	RSD (%) (n = 5)	Recovery (%)* (n = 5)
Tobacco leaf (GBW10125)	Ag (0.127), As (0.285), B (64.5), Bi (0.342), Ca (2900), Cd (0.218), Ce (1.25), Co (4.71), Cr (3.76), Cu (10.2), Fe (54), Hg (0.086), Mg (360), Mn (22.5), Mo (0.735), Ni (3.83), Pb (0.852), V (2.86), Zn (13.2)	Cd (0.202)	2.87	93-98

*The amount of cadmium added is 0.2 μg.

TABLE-4
DETERMINATION OF CADMIUM IN THE WATER SAMPLES

Samples	ICP-MS method (μg L^{-1})	Found (μg L^{-1})	RSD (%) (n = 5)	Recovery (%) (n = 5)
River water	18.2	19.1	3.2	95
Planting effluents	84.2	91.3	2.8	107

TABLE-5
COMPARISON OF REAGENTS FOR SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM

Reagent	Medium/solvent	λ_{max} (nm)	ε (× 10^4) (L mol^{-1} cm^{-1})	Linear range (μg mL^{-1})	Ref
N-Ethyl-3-carbazolecarbaxaldehyde-3-thiosemicarbazone	Acetate buffer at pH 6.0	380	0.740	0.0-12.0	7
MFPTAHK	Buffer solution of pH 6.5	420	1.28	0.0-8.0	8
tris-[2,4,6-(2-Hydroxy-4-sulpho-1- naphthylazo)]-*s*-triazine	In the pH range 5.5-7.0	510	5.0	0.2-2	9
3,5-*bis*(4-phenylazophenyl- aminodiazo)benzoic acid	pH = 10.5 buffer solution	530	18.0	0-0.5	10
Sodium diethyldithiocarbamate	CCl_4	350	4.28	0.2-2.2	11
5-(2-Hydroxy-4-nitrophenylazo)thiorhodanine	0.05-0.5 mol/L of HCl	505	15.4	0.01-2.0	This work

MFPTAHK = (N-(4-methylphenyl)-2-{[(4-phenyl-5-pyridin-4-yl-4H-1,2,4-triazol-3-yl)thio]acetyl}hydrazinecarbothioamide)

mol^{-1} cm^{-1}. It sensitive is high than that of most published reagents. By solid phase extraction with cartridge packed with MCI GEL resin, the HNSR-Cd(II) chelate in 100 mL solution can be concentrated to 1.0 mL, the enrichment fact of 100 was achieved. The detection limit reaches 0.01 μg L^{-1} in the original samples and μg L^{-1} level of cadmium can be determined with good results.

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