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Preconcentration of Maneb using Modified *β*-Cyclodextrin Polymer.

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ABSTRACT

In this study, β-Cyclodextrin polymer was synthesized and further modified with 1-(2-pyridylazo)-2-naphthol (PAN). The resulting modified polymer was used for the preconcentration of Maneb [Mn(II) ethylene bis(dithiocarbamates)] by converting it into Mn(II)-PAN-β-CDP complex. For the described method, the effect of the some analytical parameters, such as pH, adsorbent dose, contact time and eluent volume, on the % uptake of Maneb was investigated. The influence of the matrix ions and other dithiocarbamates was also examined using the developed method. The recovery values were found to be ≥95% and the relative standard deviation was ≤2%. The detection limit was found to be 1.3µg. The developed method was utilized for the preconcentration and determination of Maneb in different vegetable samples.

Keywords: Maneb; β-Cyclodextrin polymer; Functionalization; Preconcentration.

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INTRODUCTION

Introduced 40-70 years ago, dithiocarbamate fungicides (DTCs) still represent an important class widely used in agriculture. They are characterized by a broad spectrum of activity against various plant pathogens, low acute mammal toxicity, and low production costs. They are also used to manage resistance and to broaden the spectrum of activity along with the modern systemic fungicides. DTCs are also used clinically for the treatment of chronic alcoholism and as anticancer and antitoxic drug agents [1-4]. Maneb [Mn(II) ethylene bis{dithiocarbamate}] is an agricultural dithiocarbamate fungicide used on a wide variety of plant fungi and diseases. It may be applied to the foliage of plants, but it is also used for soil or seed treatment. Maneb is used primarily for almonds and stone fruits (drupes). Globally increased concern about the pesticides has induced a need to develop a highly sensitive and specific analytical method for their determinations in food, environmental and biological samples at very low concentrations. The most useful procedure, recommended by the AOAC for dithiocarbamate determination in pesticide formulations, is based on the generation of CS_2 by acid hydrolysis [5]. Dithiocarbamates have been determined using head space gas chromatography of the CS_2 evolved under controlled conditions [6], high performance liquid chromatography [7], extraction voltammetry(EV) [8]. HGC and EV are time consuming, poor sensitive and suffer from interferences. Dithiocarbamates can also be determined by other methods such as iodometry [9], EDTA [10], polarography [11], determination of the pesticides as their metallic components [12-13], derivative spectrophotometry [14], spectrophotometry [15], H-Point method [16], silica nanoparticles [17], chitin [18], naphthalene [19], flow injection spectrophotometry [20]. Maneb has also been determined by converting it into molybdenum [21] and copper [22] complexes Some more recent method for the determination of dithiocarbamate pesticides are using capillary electrophoresis [23], flow injection method [24], square wave voltammetry [25], fourier transform [26]. β-Cyclodextrin (β-CD) is a very stable oligosaccharide that is composed of seven glucose units linked with each other by α-(1,4)-glycosidic linkage. It can form supramoleculer complexes with several organic compounds by incorporating them into their hydrophobic cavities. When two or more β-Cyclodextrins are covalently linked with each other they are known as the polymers. These β-cyclodextrin polymers have been used for the preconcentration of various analytes [27-30]. Here, we have developed a relatively simple, rapid, sensitive and selective method for the determination of Maneb by converting it into a Mn(II)-PAN-β-CDP complex. In NH_3-NH_4Cl buffer solution at pH (9.5), Maneb reacts with reagent loaded on β-CDP to form a pink red colored complex. Chemical reaction between metal part of Maneb with PAN to form coloured complex has been reported which is the base for their determination.

Mn-[ethylene bis(dithiocarbamate)] + PAN = Mn-PAN + [ethylene bis(dithiocarbamate)]

EXPERIMENTAL

Apparatus

A Shimadzu UV-1800 spectrophotometer (Shimadzu Ltd., Japan) equipped with the matched 10-mm quartz cells was used to measure absorbance. All pH measurements were performed using Digital century pH-meter CP 901 with a combined glass electrode. A

thermostatic shaking water bath (Perfit India Ltd.) was used to carry out all the inclusive procedures.

Reagents

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Maneb was prepared as given in literature [31]. Its stock solution was prepared in dimethyl sulphoxide (DMSO). Further dilutions were made as and when required. 4×10^{-6} mol/L solution of the PAN reagent was prepared by dissolving an appropriate amount of PAN (Fluka Chemical Company) in N,N-dimethylformamide solvent. 1,4-Butanediol diglycidyl ether was obtained from sigma Aldrich chemical company (U.S.A.). β-Cyclodextrin was obtained from SD fine chemical India private limited (Mumbai). Buffer solution used were hydrochloric acid/ sodium acetate for pH 2.0-3.5, sodium acetate/acetic acid for pH 4.0-6.5, ammonia/ammonium chloride for pH 8-11. Glass wares were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water. Procedure

Synthesis of the β-Cyclodextrin polymer (β-CDP)

β-CDP was synthesized by known method [32]. A brief procedure for the synthesis is mentioned here. 20gm of β-CD was dissolved in 50ml of 20% NaOH. To this was added 20ml of butanediol diglycidyl ether drop wise (Figure. 2). The polymer was formed in 1.5h and dried at 90^0C. The polymer was ground and sieved first into different mesh fractions. The 80-100 mesh fraction was washed with double distilled water 5-6 times. Then, the polymer was dried again at 90˚C and kept at room temperature (25˚C) in a dessicator.

Inclusion of the PAN in the β-CDP cavity to form β-CDP-PAN modified polymer

5.0gm of the synthesized polymer, β-CDP (80-100) mesh size was taken in a 250ml Stoppard conical flask. To this was added 10ml of 9.5 pH buffer solution and polymer was allowed to swell for 15 minutes. A fixed volume of 4×10^{-6} mol/L solution of the PAN was added to the treated polymer and made 50ml with distilled water. It was shaken for two hours. The colored polymer so obtained was washed with distilled water and dried at 100˚C. The modified polymer was stored in a dessicator at room temperature for future use.

Batch extraction procedure

At room temperature i.e., 30^0C β-CDP-PAN (500mg) and 10.0 ml of buffer solution (pH 9.5) were added to a 100-ml Stoppard conical flask. The mixture was allowed to stand for approximately 15 min so that β-CDP-PAN could be swollen sufficiently. 50 µg of Maneb were added and made up to 100ml with double distilled water. After the mixture was shaken in the thermostatic shaking water bath for 45 min, 5.0ml of the supernatant solution was transferred into a 10ml volumetric flask and the absorbance was measured using standard spectrophotometric method [33]. Maneb retained on β-CDP-PAN polymer was eluted using 5.0 mL of 2M HCl.

Determination of maneb in vegetables

The method was applied for the determination of maneb in different vegetable sample. A known amount of maneb in dimethyl sulphoxide (DMSO) was crushed with 10 g. vegetable sample with the help of a pestle and mortar. The mixture was then stirred with magnetic stirrer for 1h to provide complete dissolution of maneb and then filtered to separate the food residue from the solution containing maneb. The residue was washed with DMSO to provide complete extraction of maneb to the solution. Filtrate and washings were combined and evaporated to 20.0 mL on a water bath, diluted to 100 mL with DMSO and determined by the developed method.

RESULTS AND DISCUSSION

Effect of pH

The sorption of an analyte on the chelating resin is dependent on the pH of sample solution due to the competitive reaction between chelate forming groups and hydrogen ions in the solutions [34]. An excess of Maneb 50 µg were spiked to a 100 mL of the sample solution containing 0.5 g of resin and shaken for 45 min. The pH of this solution was adjusted in the range of 2.5 to 10.5 using different buffer system and then the preconcentration procedure as described was applied. As it can be seen in (Fig. 1), quantitative uptake (≥ 95%) was obtained at pH 9.5-10.5 ± 0.01. Therefore, the working pH was chosen as 9.5 for the subsequent experiments.

Effect of the amount of adsorbent (Bed Height)

The amount of the resin is another important parameter that affects the uptake of an analyte. In order to optimize the smallest amount of extractant, 100, 200, 300, 400, 500, 600 and 700mg of the resin were added to the 100 mL of the sample solution containing 50 µg of Maneb and preconcentrated by the general procedure. The quantitative recoveries were obtained for and above 500 mg of resin (Fig. 2). Therefore, 500 mg of the resin has been used for subsequent experiments.

Effect of shaking time

Shaking time is an important factor in determining the possibility of application of the β-CDBP-PAN polymer for the uptake of maneb. For studying the effect of shaking time on the % uptake, a 0.5 g amount of resin was stirred with 100 ml of solution containing 50 µg of maneb for different shaking time (ranging from 15, 30, 45, 60, 75) min at optimum pH. The results of % uptake of maneb vs. the shaking time show that the percentage uptake reached maximum (above 95%) at 45 min (Fig. 3). Therefore, the shaking time of 45 min. was selected as the adsorption equilibrium time.

Effect of elution conditions

Optimization of the elution conditions were performed in order to obtain the maximum recovery with the minimal concentration and volume of the eluent. Different

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concentrations of HCl ranging from (0.5-4M) were tested in order to strip the Maneb from resin. The experimental results showed that 2M HCl was sufficient for complete elution of Maneb. It was found that quantitative recoveries (≥95%) were obtained with 5.0 mL of 2.0M HCl as eluent (Fig. 4). The time needed for complete desorption was 30 seconds.

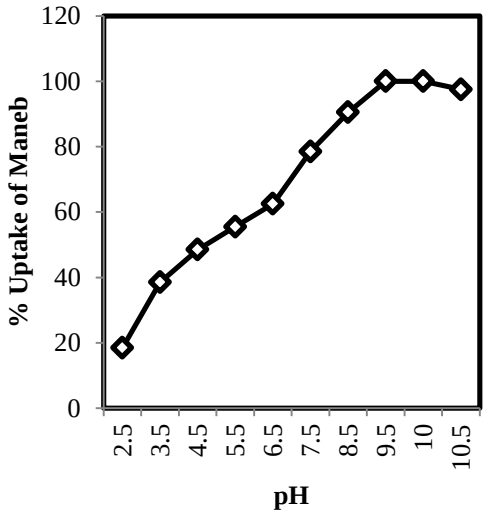

Fig. 1. Effect of pH

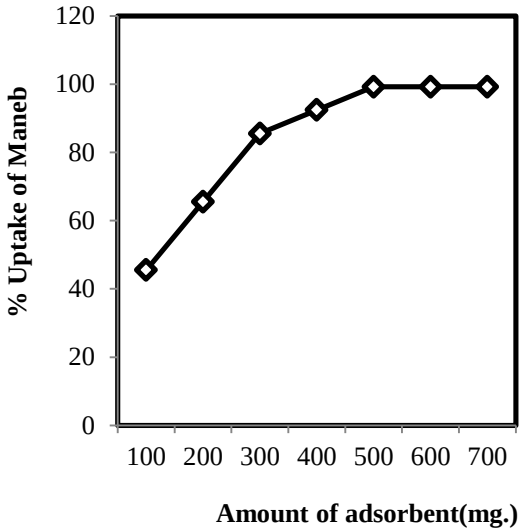

Fig. 2. Effect of adsorbent dose

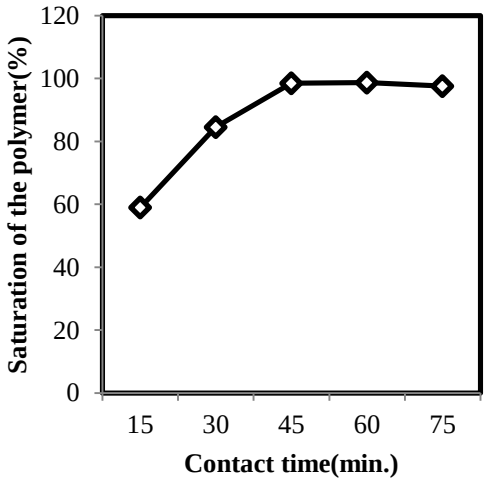

Fig. 3. Effect of the contact time

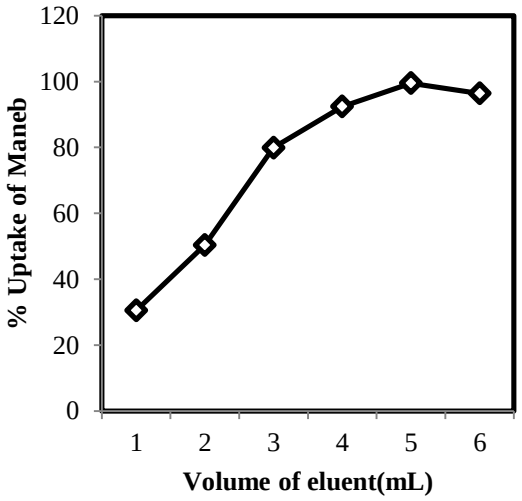

Fig. 4. Effect of eluent volume

Applications of the method

The method was applied to determination of Maneb in different vegetable samples. The results are shown in table 1.

Table 1: Determination of Maneb in vegetable samples (n=3)

Sample	Spiked(µg.)	Found(µg.)	% Relative Error	% Recovery ± R.S.D.(%)

Tomato	0.0	N.D.	-------	--------
	20.0	19.6	2.0	98.0 ± 1.3
	40.0	39.2	2.0	98.0 ± 1.3
Potato	0.0	N.D.	--------	--------
	50.0	49.5	1.0	99.0 ± 1.0
	45.0	44.4	1.3	98.6 ± 0.8
Cucumber	0.0	N.D.	--------	--------
	35.0	34.4	1.7	98.3 ± 1.2
	55.0	54.4	1.1	98.9 ± 1.0

N.D. (not detected)

CONCLUSIONS

The proposed preconcentration method consists of a simple and low cost procedure which permits the quantitative recovery of Maneb from vegetable samples. The chelating polymer has been used along all the experiments performed for this study. The recovery values were found to be ≥95% and the relative standard deviation was ≤2%. The LOD was found to be 1.3µg and LOQ was 4.1.µg. The method has an enrichment factor of 70.

REFERENCES

[1] Chen D, Cui QC, Yang H, Dou QP. Cancer Res 2006;66:10425.
[2] Viola M, Rieber MS, Rieber M. Biochem Pharmacol 2006;71:722.
[3] Frank N, Christmann A, Frei E. Toxocology 1995;95:113.
[4] Vettorazzi G, et al. Teratog Carcinog Mutagen 1995;15:313.
[5] Clarke DG, Baum H, Stanley EL, Hester WE. Anal Chem 1951;23:1842.
[6] McLeod HA, McCulley KA. J Assoc Off Anal Chem 1969;52:1226.
[7] Gustafsson KH, Falhgren CH. J Agric Food Chem 1983;31:461.
[8] Valkanovich NA, Medyantseva ED, Frolova VF, Romanova ON. Zh Anal Khim 1983;38: 1963.
[9] Clyde DD. J Assoc Off Anal Chem 1983; 66: 646.
[10] Hyman AS. Analyst 1969;94:152.
[11] Halls DJ, Townshend A, Zumen P. Analyst 1968;93:219.
[12] Quintero MC, Silva MD. Talanta 1991;38:359.
[13] Ruiz T, Lozano C, Tomas V, Casajus R. Talanta 1996;43:193.
[14] Malik AK, Bansal S, Aulakh JS. Anal Bioanal Chem 2002;375:1618.
[15] Zaijun L, You F, Zhongyun L, Jian T. Talanta 2004;63:647.
[16] Kaur PP, Gupta U. E J Chem 2009;6:106.
[17] Kaur A, Gupta U. Eurasian J Anal Chem 2011;6:1.
[18] Mehta SK, Malik AK, Singh B, Rao ALJ. Talanta 2005;67:725.
[19] Malik AK, Sharma V, Sharma VK, Rao ALJ. J Agric Food Chem 2004;52:7763.
[20] Perez-Ruiz T et al. Microchim Acta 2003;142:231.
[21] Rao ALJ, Verma N J Indian Acad Forensic Sci 1985;24:1.
[22] Rangaswamy JR, Poornima P, Majumdar SK. J Assoc Off Anal Chem 1970;53:1043.
[23] Malik AK, Faubel W. Talanta 2000;52:341.
[24] Paz JLL, Icardo MC. Anal Chim Acta 2008;625:173.
[25] Qiu P, Ni YN. Chin Chem Lett 2008;19:1337.
[26] Cassella AR, Garrigues S, De Campos RC, Guardia M. Talanta 2001;54:1087.
[27] Abay I, Denizli A, Biskin E, Salih B. Chemosphere 2005;61:1263.
[28] Shao D et al. Chemosphere 2010;79:679.

[29] Wu M, Zhu X. Spectrochim Acta A Mol Biomol Spectrosc 2010;77:1021.
[30] Bhaskar M, Aruna P, Radhakrishnan G. Anal Chim Acta 2004;509:39.
[31] Kapoor J, Rao ALJ. Pestic Sci 1994;42:109.
[32] Komiyama M, Hirai H. Polym J 1987;19:773.
[33] Toral MI, Lara N, Narvaez J, Ricter PJ. J Chil Chem Soc 2004;49:163.
[34] Minami T, Atsumi K, Ueda J. Anal Sci 2003;19:313.