

Preconcentration of Ferbam [Fe(III) tris(dimethyldithiocarbamate)] Using 1-(2-Pyridylazo)-2-naphthol Modified β -Cyclodextrin Polymer

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Abstract: In this study, β -Cyclodextrin polymer functionalized by 1-(2-pyridylazo)-2-naphthol (PAN) was synthesized and the resulting modified polymer was used for the preconcentration of Fe(III) tris(dimethyldithiocarbamate) by converting it into Fe(III)-PAN- β -CDP complex. For the described method, the effect of some analytical parameters, such as pH, sample volume, contact time and volume of the eluent, on the recovery of Fe(III) tris(dimethyldithiocarbamate) were investigated. The recovery values were found to be $\geq 95\%$. The developed method was utilized for the preconcentration and determination of Ferbam in different water samples.

Keywords: Ferbam, β -Cyclodextrin polymer, Functionalization, Preconcentration.

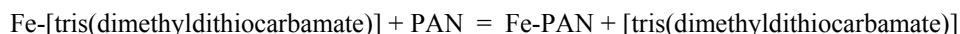
Introduction

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 agents¹⁻⁴. Ferbam [Fe(III) tris{dimethyldithiocarbamate}], [$\{(CH_3)_2NCS_2\}_3Fe$] 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. Ferbam is used primarily for almonds and stone fruits (drupes). There is a number of methods available in the literature for the determination of dithiocarbamates. One of such method explains about the determination of Ferbam by its decomposition into amine and carbon disulphide⁵. Ferbam is determined by converting it into molybdenum⁶ and copper⁷ complexes. Dithiocarbamates have been determined using head space gas chromatography of the CS_2 evolved under controlled conditions⁸, high performance liquid chromatography⁹, extraction voltammetry(EV)¹⁰. HGC and EV are time consuming, poor sensitive and suffer from interferences. Dithiocarbamates can also be determined by other methods such as iodometry¹¹, EDTA¹², polarography¹³, determination of the pesticides as their metallic components¹⁴⁻¹⁵, derivative spectrophotometry¹⁶,

spectrophotometry¹⁷, *H*-Point method¹⁸, silica nanoparticles¹⁹, chitin²⁰, naphthalene²¹, flow injection spectrophotometry²². All of the above mentioned methods suffer from one or more disadvantages:

- (a) Methods other than gas chromatography (GC) are indirect and time consuming, and their sensitivity is quite low.
- (b) GC methods are sensitive but suffer from lack of selectivity because all dithiocarbamates pesticides evolve carbon disulphide on acid hydrolysis.
- (c) HPLC methods are less sensitive than GC methods, they require a longer time for analysis and use of organic solvents as mobile phase and are relatively expensive.

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 supramolecular 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 analytes²³⁻²⁶. Here, we have developed a relatively simple, rapid, sensitive and selective method for the determination of Ferbam by converting it into a Fe(III)-PAN- β -CDP complex. In AcOH-NaoAc buffer solution at pH 5.5, Ferbam reacts with reagent loaded on β -CDP to form an earthy red colored complex. Chemical reaction between metal part of Ferbam with PAN to form coloured complex has been reported which is the base for their determination.



Experimental

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Ferbam was prepared as given in literature²⁷. 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. Glassware were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water. 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.

Procedure

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

β -CDP was synthesized by known method²⁸. A brief procedure for the synthesis is mentioned here. 20 g of β -CD was dissolved in 50 mL of 20% NaOH. To this 20 mL of butanediol diglycidyl ether was added drop wise. The polymer was formed in 1.5 h and dried at 90 °C. The polymer was ground, sieved and 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 desiccator.

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

5.0g of the synthesized polymer, β -CDP was taken in a 250 mL stoppered conical flask. To this 10 mL of 9.5 pH buffer solution was added 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 50 mL 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 °C β -CDP-PAN (500 mg) and 10.0 mL of buffer solution (pH 9.5) were added to a 100 mL stoppered conical flask. The mixture was allowed to stand for approximately 15 min so that β -CDP-PAN could be swollen sufficiently. 75 μ g of Ferbam were added and made up to 100 mL with double distilled water. After the mixture was shaken in the thermostatic shaking water bath for 45 min, 5.0 mL of the supernatant solution was transferred into a 10 mL volumetric flask and the absorbance was measured using standard spectrophotometric method²⁹. Ferbam retained on β -CDP-PAN polymer was eluted using 5.0 mL of 2M HCl.

Sample collection and conditioning

Water samples were collected from the different parts of Patiala City, India. The water samples were immediately filtered through cellulose membrane filter (0.45 nm pore size), and stored in pre-cleaned polyethylene bottles. After then, pH of the sample was adjusted to 5.5 and the preconcentration procedure as described above was applied

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 solutions³⁰. 75 μ g of Ferbam were spiked to a 100 mL of the model solution. The pH of this solution was adjusted in the range of 2.5 to 10.5 using different buffer solutions and then the preconcentration procedure as described was applied. As it can be seen in Figure 1, quantitative uptake ($\geq 95\%$) was obtained at pH 5.5. Therefore, the working pH was chosen as 5.5 for the following 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 selective uptake of Ferbam. Different shaking time (ranging from 15 to 75min) were studied for the % uptake of Ferbam by β -CDP-PAN polymer. The results of % uptake of Ferbam *vs.* the shaking time show that the percentage uptake reach maximum (above 95%) at 45 min (Figure 2). Therefore, the shaking time of 45 min. was selected as the adsorption equilibrium time.

Effect of the sample volume

In order to explore the possibility of enriching low concentration of analytes from large volume of solution, the effect of sample volume on the retention of Ferbam was also investigated. For this purpose, 25, 50, 100, 150, 200, 250, 300, 350 and 400 mL of sample solutions containing 75 μ g of Ferbam were taken. Quantitative uptakes ($\geq 95\%$) were obtained for sample volume of ≤ 300 mL (Figure 3). Therefore, 100 mL of sample solution was adopted for the preconcentration of analyte from sample solutions.

Effect of elution conditions on recovery

Since the adsorption of Ferbam at $\text{pH} \leq 2$ is quite low, one can expect that elution will be favored in the acidic solutions. So various concentrations and volumes HCl were used for the desorption of retained Ferbam. The experimental results showed that 2M HCl was sufficient for complete elution of Ferbam. It was found that quantitative recoveries ($\geq 95\%$) with 4.0 mL of 2.0M HCl as eluent could be obtained (Figure 4). Therefore, for eluting Ferbam 4.0 mL of 2.0M HCl was used as eluent.

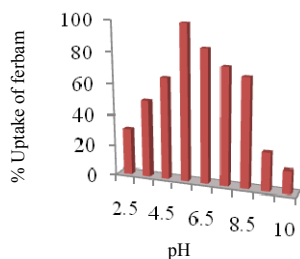


Figure 1. Effect of pH on the % uptake of Ferbam

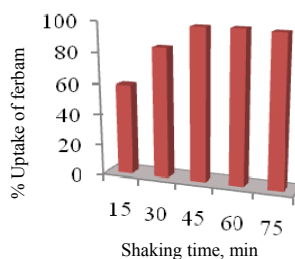


Figure 2. Effect of the contact time on the % uptake of Ferbam.

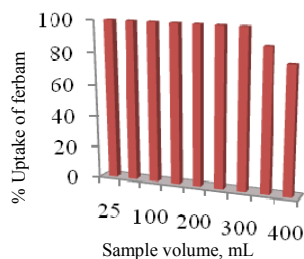


Figure 3. Effect of the sample volume on the % uptake of Ferbam

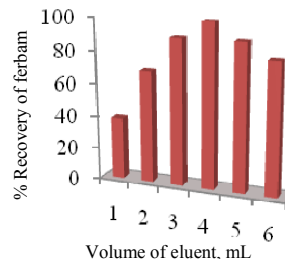


Figure 4. Effect of eluent volume on % uptake of Ferbam

Applications of the method

The method was applied to the determination of Ferbam in different water samples. The results are given in the Table 1. The accuracy of the described preconcentration method was tested in the recovery studies by adding known amounts of Ferbam to the water sample. The recovery values obtained from the water samples were satisfactory. These results confirm the validity of the proposed method.

Table 1. Determination of Ferbam in different water samples, (n=3)

Sample	Spiked, μg .	Found, μg .	% Relative Error	% Recovery \pm R.S.D., %
Tap Water	0.0	N.D	-	-
	15.0	14.7	2.9	97.1+2.1
	20.0	19.5	2.5	97.5+1.5
Bore Water	0.0	N. D.	-	-
	35.0	34.0	1.0	99.0+1.0
	40.0	38.7	1.7	98.3+1.2
River Water	0.0	N.D	-	-
	55.0	54.6	1.0	99.0+1.0
	65.0	64.4	1.0	99.1+1.0

N.D. (not detected)

Conclusion

The proposed preconcentration method consists of a simple and low cost procedure which permits the quantitative recovery of Ferbam from water and vegetable samples. Owing to the synthesized chelating polymer having high affinity for Ferbam, its selective determination is possible. The chelating polymer has been used along all the experiments performed for this study. Because of that it has superior reusability. The recovery values were found to be $\geq 95\%$. The method has an enrichment factor of 75.

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