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Spectrophotometric determination of the fungicides captan and folpet in their commercial formulations

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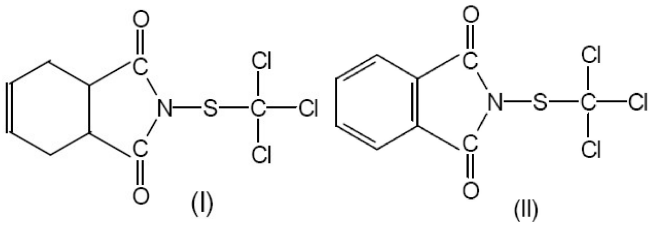
Abstract : Captan and folpet react with thiophenol in the presence of triethylamine in acetonitrile to form a bis (phenyl) trithiocarbonate which reacts with 2, 4-dinitrophenyl hydrazine in the presence of hydrochloric acid to form corresponding hydrazone. The latter is transformed into an intense red quinoidal ion immediately on making solution alkaline. This observation have been made the basis of a simple spectrophotometric method for the determination of above fungicides. The red colour is stable for at least 6 hrs and shows λ_{max} at 510 nm using either fungicide. The method has been successfully applied to the analysis of above fungicides in their commercial formulations samples.

Keywords : Spectrophotometric method; bis (phenyl) trithiocarbonate; direct colorimetric procedure; residue analysis

INTRODUCTION

Captan [N-(trichloromethylthio) tetrahydrophthalimide, I] and folpet [N- (trichloromethylthio) phthalimide, II] have found a variety of application in agriculture as fungicides. They are recommended both as disinfectants and protectants of grains. They are also effective for the control of apple scab.

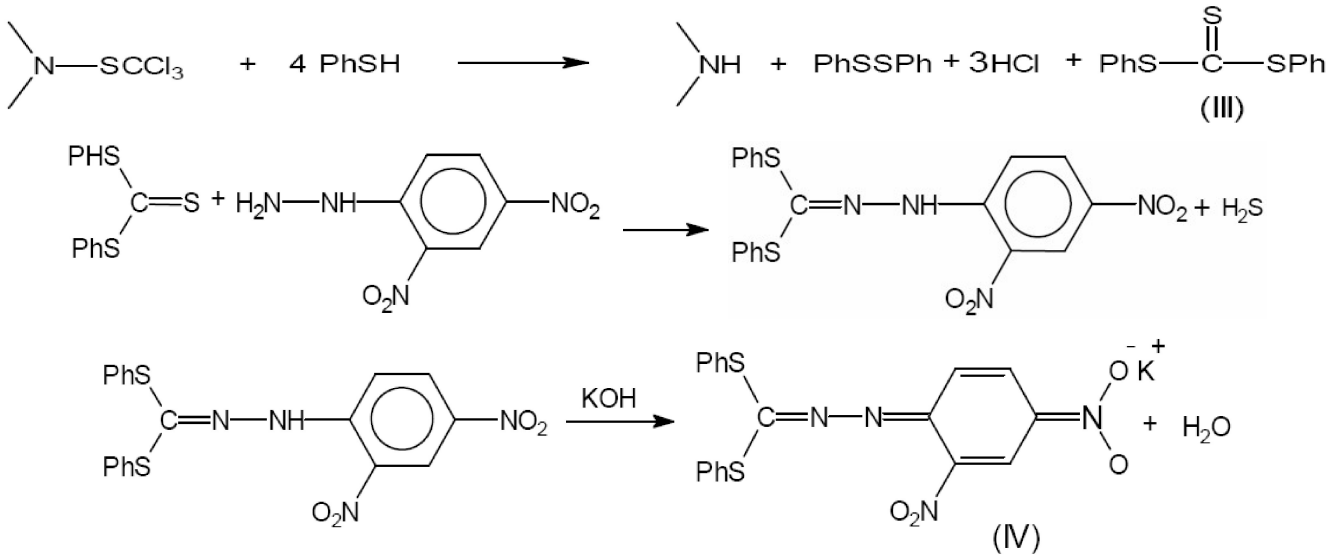


(I) (II)

The colorimetric method[1] commonly employed for their determination at residue level consists in heating the fungicide solution in benzene with resorcinol at 140 ^{0}C for 25 min followed by its acidification with acetic acid to form yellow colour which is measured at 428 nm. The method is tedious, time -consuming and requires a number of steps with strict control of experimental conditions particularly with regard to the protection of reaction products from moisture (It has been observed that one drop of water may cause an apparent loss of 20 % of the fungicide). This, therefore, calls for a simple and sensitive method for formulation and residue analysis of captan and folpet. Advantage has been taken of the following observations to accomplish the task.

i) Each fungicide reacts with thiophenol in the presence of triethylamine in acetonitrile to form yellow soluble bis (phenyl) trithiocarbonate (III). The validity of this reaction has been established in our laboratory[2].

ii) Bis (phenyl) trithiocarbonate (III)) reacts with 2,4-dinitrophenyl hydrazine in methanol to form the



corresponding hydrazone. Though the latter is formed in acidic solution but on adding alkali, an intensely red solution, (presumably because of the formation of resonating quinoidal ion (IV)), results.

iii) This coloured solution shows λ_{max} at 510 nm and is stable for at least 6 hrs.

The method consists in reacting each fungicide with thiophenol in the presence of triethylamine in acetonitrile followed by the addition of 2,4-dinitrophenyl hydrazine (in methanol) and a drop of concentrated hydrochloric acid. Each solution is then made alkaline by the addition of potassium hydroxide solution and the resulting colour measured at 510 nm spectrophotometrically. The method has been successfully adapted to the analysis of captan and folpet in their formulated products and residues on agricultural produces viz grains and apple fruits.

EXPERIMENTAL

Reagents

Acetonitrile (Merck) was distilled twice from phosphorous pentoxide (5 gl^{-1}).

Triethylamine (SRL, Extrapure AR) was used as such for preparing 1M solution in acetonitrile.

Thiophenol (Reidel, German) was distilled before use. Its standard solution was prepared by dissolving a little more than the calculated amount of the compound in acetonitrile and standardizing the solution by reported method[3].

Methanol (BDH) was distilled over magnesium[4].

Potassium hydroxide: Its 10% solution in methanol was used.

2,4- Dinitrophenyl hydrazine (SRL) was recrysatllised before its use. Its standard solution was prepared by dissolving a little more than the calculated amount in methanol and standardizing it by the reported method[5]

Eluting solvent: A mixture of equal volumes of cyclohexane and diethyl ether (Glaxo) was used.

Silica gel (60-120 mesh, Sisco Research) was heated at 500 ^{0}C for 4 h, cooled and stored at 120 ^{0}C.
Captan and Folpet: The high purity standards of captan and folpet were supplied by EPA, USA.

Apparatus

A Bausch and Lomb spectrophotometer (Spectronic 20 D) with 1 cm matched glass cells was used for absorption measurements.

Procedures

Direct colorimetric procedure

Preparation of calibration curve for compounds

Aliquots (0.1- 1.0 ml) of standard solutions of each compound in acetonitrile were added to glass stoppered conical flasks containing triethylamine (0.5 ml, 0.1M in acetonitrile) and thiophenol (0.5 ml, 0.1 M in acetonitrile) and volume made to 4 mL with acetonitrile. Each solution was mixed with 2,4-dinitrophenyl hydrazine reagent (1 ml, 0.002 M in methanol) and a drop of concentrated hydrochloric acid. Each flask was stoppered loosely and heated on a water bath at 50 ^{0}C for

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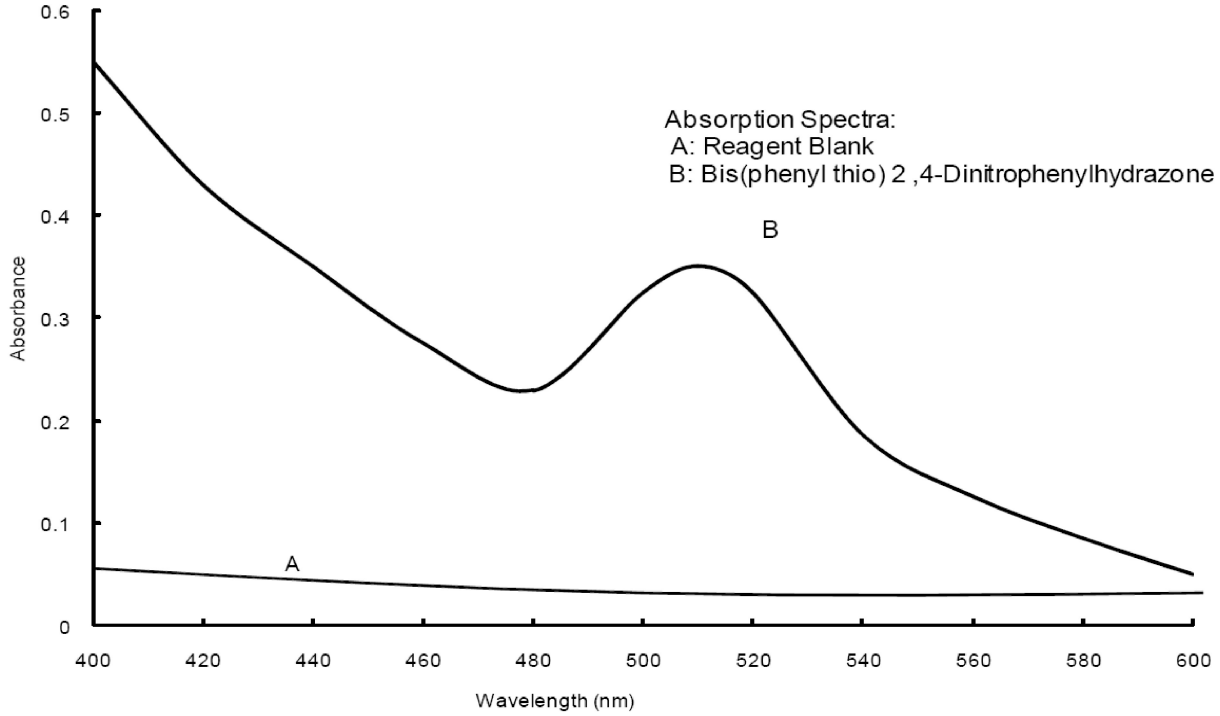

Figure 1

5 min to ensure the completion of reaction. The contents of flasks were cooled to room temperature (~24 ^{0}C) and transferred to a 10 mL - measuring flask and the volume made upto the mark with potassium hydroxide (10 % solution in methanol). The absorbance of red solution so obtained was measured at 510 nm (λ_{max} of red colour, Figure 1) against blank, and calibration curve prepared in each case. The relationship between concentration of each fungicide and absorbance was linear upto 15 μg /mL.

(A) Formulation analysis

Two captan formulations (one containing 75% and the other containing 50 % active ingredient) and one folpet formulation (containing 50 % active ingredient), all wettable powders, were used.

A single large sample of each formulation was weighed, shaken with acetonitrile and filtered. The residue was washed 2-3 times with acetonitrile. The filterate and washings were diluted to a known volume with the same solvent. Aliquots of this solution were then taken and the analysis was carried out as described above for pure compounds. Assay results are given in TABLE 1.

(B) Residue analysis

(a) Recovery experiments

Various amounts of each fungicide in acetonitrile were added to 5 gm of grains (wheat and Maize). The samples were mixed thoroughly and extracted 5 times, each time using 2-3 ml of acetonitrile, in glass stoppered conical flasks containing triethylamine (0.5 ml, 0.1M in acetonitrile) and thiophenol (0.5 ml, 0.1M in acetonitrile) and volume made to 10 ml with acetonitrile. To each solution was added 2,4-dinitrophenyl hydrazine (1ml, 0.002 M in methanol) and a drop of concentrated hydrochloric acid and the contents heated on a water bath at 50 ^{0}C for 5 min, brought to room temperature and transferred to a 25 ml-measuring flask. Finally, each solution was mixed with potassium hydroxide (5 ml, 10 % solution in methanol) and the final volume made upto the mark with methanol. The red colour thus obtained was evaluated at 510 nm against a reagent blank. Assay results are given in TABLE 2.

TABLE 1 : Assay results of commercial formulation of captan and folpet.

Fungicide formulation	Based on active ingredient (%)	Active ingredient found, * %	
		Present method	Comparison method
Captan I	75	74.9 ± 0.5	74.2 ± 0.6
Captan II	50	49.4 ± 0.4	49.6 ± 0.6
Folpet I	50	49.7 ± 0.5	49.6 ± 0.5

*** Values are mean of five determinations with standard deviation (±)**

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TABLE 2 : Recovery of fungicides from fortified grain and samples.

Fungicide	Added (µg)	Recovery, * %		
		Wheat	Maize	Apple fruit
Captan	2.0	95.3 ± 0.46	96.2 ± 0.48	93.2 ± 0.81
	4.0	94.6 ± 0.52	94.8 ± 0.74	92.1 ± 0.78
	6.0	94.2 ± 0.42	94.2 ± 0.52	90.9 ± 0.69
	8.0	96.2 ± 0.60	96.8 ± 0.60	91.9 ± 0.58
	15.0	94.8 ± 0.42	96.4 ± 0.58	93.4 ± 0.62
Folpet	3.0	93.2 ± 0.54	95.4 ± 0.58	92.2 ± 0.72
	6.0	94.1 ± 0.48	95.2 ± 0.68	91.6 ± 0.68
	9.0	93.8 ± 0.64	93.8 ± 0.46	93.2 ± 0.64
	12.0	95.1 ± 0.68	94.6 ± 0.42	91.4 ± 0.58
	15.0	96.2 ± 0.56	95.1 ± 0.70	93.6 ± 0.62

*** Values are mean of five determinations with standard deviation (±)**

In case of apple fruits, known weighed samples (20g) placed in glass containers were sprayed with various amounts of standard fungicide solution (in acetonitrile). The samples were well mixed and blended mechanically with a Teflon-bladed stirrer with 100ml of acetonitrile in the same container for 3 min and passed through a Buchner funnel fitted with a sintered glass filter. The residue of each sample was washed 5 times with acetonitrile and the combined extracts were cleaned up on silica gel column topped with 2 g anhydrous sodium sulphate (a drying agent to prevent absorption of atmospheric moisture). The elute was concentrated by evaporation. The residue was dissolved in acetonitrile and processed for analysis as described in case of grains. The results are given in TABLE 2.

TABLE 3 : Results of residue analysis of treated samples.

Fungicides	Strength of Spray used (gl^{-1})	Fungicide residue found, (ppm)		
		Wheat	Maize	Apple fruits
Captan*	8	35.2	30.6	28.6
	4	22.9	18.9	15.4
	2	8.4	8.2	9.4
	1	5.8	5.2	6.6
Folpet**	8	32.2	28.3	25.2
	4	18.4	18.8	14.2
	2	9.8	10.2	8.2
	1	6.4	4.2	3.4

***Formulation based on 75 % active ingredient.**
****Formulation based on 50 % active ingredient.**

(b) Residue analysis

Grains (wheat and maize) and apple fruits were sprayed with each fungicide formulation (aqueous dispersion) at a concentration of 1- 8 gl^{-1} at a rate 100ml kg^{-1} commodity. Sprayed samples were dried in the sun and from these lots, samples of 15-20 gm were taken for residue analysis and processed as described under recovery experiments. The results are given in TABLE 3.

RESULTS AND DISCUSSION

The proposed colorimetric method for the determination of captan and folpet is quite sensitive (ε values for red bis (phenyl) 2,4-dinitrophenyl hydrazone formed from captan and folpet are 3.21×10^3 and 3.16×10^3 l mol^{-1} cm^{-1} respectively on the basis of respective fungicide contents); as little as 1 µg ml^{-1} of each fungicide can be determined. When applied to the analysis of commercial formulations of these fungicides, the recoveries were in the range 98.8 - 99.8 % of the nominal content with RSD's in the range 0.4 - 0.5 % (TABLE 1). Recoveries of these fungicides from fortified grains and apple fruit sample ranged from 90.9 -96.8 % with RSD's in the range 0.42 -0.81 % (TABLE 2). Results of residue analysis (ppm) of treated samples are given in TABLE 3.

The simplicity of the procedure, excellent solution stability of red colour and non-requirement of extraction of coloured products are some attractive features of the proposed method.

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