

A NEW REDUCTIMETRIC METHOD FOR THE DETERMINATION OF CAPTAN AND FOLPET IN THEIR FORMULATIONS

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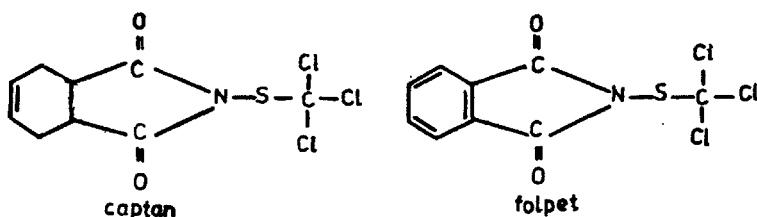
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A new simple, accurate and reliable titrimetric method for the determination of captan and folpet based on the reductive cleavage of their N-S -bond by a dithiocarbamate, is described. The analysis is concluded by measuring the residual dithiocarbamate by iodine monobromide titration. The method has been successfully adapted to the analysis of some commercial formulations of captan and folpet. It is recommended for routine analysis of such formulations.

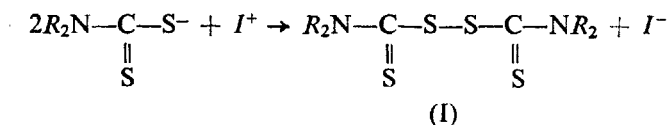
Key Words : Captan; Folpet; Fungicides; Dithiocarbamates; Potentiometry; Formulation Analysis; Iodine Monobromide; Dibutylamine; Carbon Disulphide

INTRODUCTION

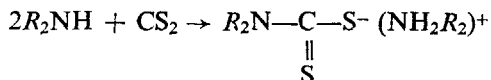
CAPTAN, N-(trichloro-methyl-thio) tetrahydrophthalimide and folpet, N-(trichloro-methyl-thio) phthalimide form an important class of organic synthetic



fungicides occupying an eminent position among modern agro-chemicals. These compounds are characterised by the presence of N-S -bond. The ease with which a dithiocarbamate smoothly and quantitatively cleaves this bond, has afforded us a simple, accurate and reliable method for the determination of captan and folpet. The method consists in reacting each fungicide with a known excess of a dithiocarbamate in acetonitrile and measuring the residual dithiocarbamate oxidimetrically through titration with iodine monobromide. Acetonitrile



has been chosen as solvent because, (i) each fungicide is soluble in acetonitrile; (ii) a dithiocarbamate to be used as reagent can be quantitatively generated in acetonitrile by reacting a calculated amount of an amine with an excess of carbon



disulphide. That the above reaction indeed proceeds quantitatively has already been established in our laboratory;^{1,2} (iii) iodine monobromide solution in acetonitrile shows good stability;³ and (iv) the determination of dithiocarbamates by oxidimetric methods in non-aqueous medium is advantageous.^{3,4}

The proposed method has been successfully adapted to some commercial formulations based on above compounds i.e., captan and folpet.

MATERIALS AND METHOD

Acetonitrile (E. Merck) was distilled twice from phosphorus pentoxide (5g/l).

Dibutylamine (Fluka-Switzerland) was distilled before use.

Carbon disulphide (Baker analysed) was used as received.

Iodine monobromine (0.05N in acetonitrile). The compound was prepared⁵ and its solution standardised⁶ as reported earlier.

Captan and folpet : The standards of high purity were supplied by the courtesy of Environmental Protection Agency, NC, USA.

Potentiometric titrations were performed with a Toshniwal CL06A potentiometer using a bright platinum wire indicator electrode and modified-calomel (saturated methanolic potassium chloride solution used instead of aqueous) reference electrode.

Procedure

Determination of Captan and Folpet—Aliquots of solutions in acetonitrile of each pure compound were added dropwise to the titration vessels containing dibutylamine (5ml, 0.1N) in acetonitrile, 2–3 drops of carbon disulphide (to convert the amine to dithiocarbamate) and 25 ml of acetonitrile. There was appearance and immediate disappearance of yellow colour during the addition of each compound. Finally, the colourless solutions were titrated at room temperature (~ 23°) with standard (0.05N) iodine monobromide visually and potentiometrically. In visual titrations, the end-point was marked by the appearance of yellow colour imparted to the solution by the first drop of the oxidant added in excess. In

TABLE I
Determination of captan and folpet

Captan taken (mg)	Agrochemical found*, (mg)		
	Present method		Hydrolysis method
	Visual method	Potentiometric method	
1.00	0.99, 0.005	1.01, 0.004	1.01, 0.007
3.00	2.97, 0.018	3.01, 0.016	3.03, 0.031
5.00	5.04, 0.035	4.97, 0.030	4.95, 0.052
7.00	7.03, 0.042	6.96, 0.040	6.95, 0.072
10.00	9.94, 0.058	9.96, 0.060	10.08, 0.089
Folpet taken (mg)			
1.00	1.00, 0.006	0.99, 0.005	1.01, 0.008
2.00	1.98, 0.012	2.02, 0.010	1.98, 0.035
4.00	4.02, 0.020	3.97, 0.018	3.96, 0.073
8.00	8.05, 0.036	7.94, 0.032	8.06, 0.062
10.00	9.94, 0.060	9.95, 0.057	9.92, 0.088

*Values are mean of ten determinations with standard deviation (\pm).

potentiometric titrations, a sharp jump in the potential was observed at the end-point. The results are given in Table I.

Formulation Analysis

Three captan formulations (two containing 75 per cent active ingredient each and one containing 50 per cent active ingredient) and one folpet formulation (containing 50 per cent 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 2-4 times with acetonitrile. The filtrate and washings were made upto the known volume with the same solvent. Aliquots were taken in titration vessels for analysis. The visual and potentiometric titrations were performed in the same manner as described above for pure compounds. The results are given in Table II.

RESULTS AND DISCUSSION

The chemical method commonly described for the analysis of captan and folpet involves their selective hydrolysis⁷ followed by halide determination. It is based upon differential rates of hydrolysis of the parent compound versus the chloride containing impurities derived from perchloromethyl mercaptan. Perchloromethyl mercaptan as well as other impurities derived from this chemical hydrolyse very rapidly in acetone-methanol solution to yield chloride ion. The total chloride content is then determined by sodium hydroxide hydrolysis. The difference between

TABLE II
 % Recovery of captan and folpet from their technical formulations

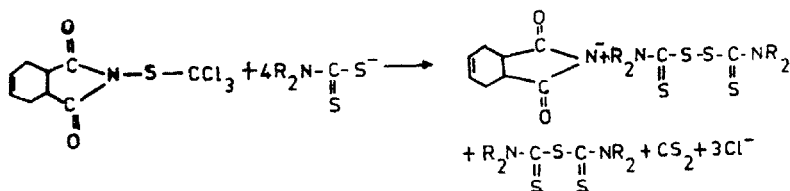
Fungicide formulation	Based on active ingredient (%)	Amount taken, (mg)	Amount found*, mg					
			Present method			Hydrolysis method		
			Visual	Recovery, %	Potentiometric Recovery, %	Visual	Recovery, %	Hydrolysis Recovery, (%)
Captan	50	2.00	1.97	98.5, 0.32	1.98	99.0, 0.30	1.98	99.0, 0.34
		20.00	19.48	97.4, 0.44	19.52	97.6, 0.42	1.96	98.1, 0.47
Captan	75	2.00	1.93	96.5, 0.36	1.95	97.5, 0.35	1.94	97.3, 0.42
		12.00	11.73	97.7, 0.32	11.75	97.9, 0.30	11.74	97.8, 0.32
Folpet (Phaltan)	50	3.00	2.96	98.6, 0.48	2.95	98.2, 0.44	2.46	98.6, 0.50
		15.00	14.80	98.7, 0.42	14.82	98.8, 0.43	14.76	98.4, 0.45
Folpet (Phaltan)	50	2.00	1.94	97.0, 0.47	1.96	98.0, 0.45	1.94	97.2, 0.49
		20.00	19.76	98.8, 0.44	19.78	98.9, 0.42	19.74	98.7, 0.48

*Values are mean of ten determinations with standard deviation (\pm)

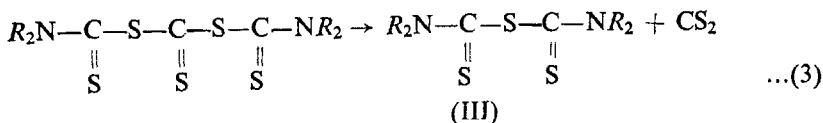
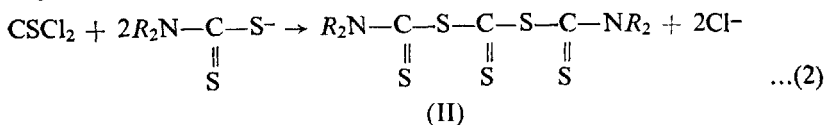
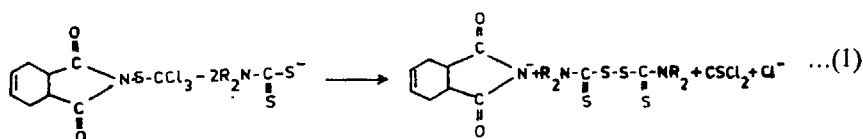
total chloride ion and impurity chloride ion is calculated as pure agrochemical. The method besides being tedious and time-consuming, requires strict control of experimental conditions. Moreover, the complete analysis cannot be conducted with a single portion of test solution; two similar aliquots are required.

The proposed method besides being simple, accurate and reliable is advantageous in that the whole analysis is conducted with a single portion of the test solution. An attractive feature of the method is that the dithiocarbamate reagent can be quantitatively generated in acetonitrile itself by reacting calculated amount of an amine with an excess of carbon disulphide. This saves the labour not only of synthesis and purification of the reagent but its protection from atmospheric oxygen as well.

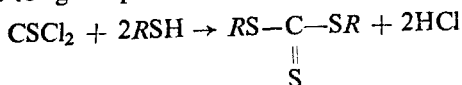
Each molecule of the fungicide consumes four equivalents of dithiocarbamate. The overall reaction with the captan may be written as :



The most plausible pathways for the reaction are :



The yellow colour which appears on adding the agrochemical to the reagent is presumably due to intermediate(II) which decomposes immediately to give thiuram monosulphide(III) and carbon disulphide. The formation of (II) is supported by the work of Owens and Blaak,⁸ who showed that thiophosgene reacts with sulphhydryl compounds to give products of type II (and dithiocarbamates do behave as



sulphydryl compounds/ion). This has been established by spectral and elemental analysis of such products.⁸ That these products are unstable when dithiocarbamates are used, has also been mentioned.^{8,9} The liberation of one mole of carbon disulphide measured by a colorimetric method¹⁰ developed in our laboratory further lends support to this point.

Iodine monobromide titrations of the residual dithiocarbamate can be performed visually (without any indicator) and potentiometrically. Although for most purposes the visual end-point is adequate, the potentiometric method is useful when the sample solution is coloured. The proposed method has first been applied to pure samples of captan and folpet. The results recorded in Table I show that captan and folpet in the range from 1 to 10mg can be determined with maximum relative standard deviation of 0.7 per cent. The method was subsequently applied to some commercial formulations (based on captan and folpet) to analyse them for their active ingredient contents. The recoveries (Table II) which are in the range of 96.5 to 99.0 per cent with standard deviations in the range of 0.3 to 0.5 per cent indicate the high accuracy and reproducibility of the proposed titrimetric method.

ACKNOWLEDGEMENT

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