Journal of Advances in Science and Technology

Vol. IV, Issue No. VII, November-2012, ISSN 2230-9659

H-POINT STANDARD ADDITION METHOD FOR SIMULTANEOUS DETERMINATION OF MANEB AND ZINEB

AN INTERNATIONALLY INDEXED PEER REVIEWED & REFEREED JOURNAL

www.ignited.in

Journal of Advances in Science and Technology
Vol. IV, Issue No. VII, November-2012, ISSN 2230-9659

H-Point Standard Addition Method for Simultaneous Determination of Maneb and Zineb

Raghvendra Rao Sanapala

Research Scholar, CMJ University, Shillong, Meghalaya

Abstract – The H-point standard addition method (HPSAM) has been applied for simultaneous determination of maneb and zineb using 1-(2-pyridylazo)-2- naphthol (PAN) as a reagent. Both maneb and zineb form wine red colored complex with PAN at pH 9.2 which are soluble in Triton X-100. Zineb and maneb can be determined simultaneously in the range of 0.414-3.446 µg mL-1 and 0.663-3.316 µg mL-1respectively with satisfactory accuracy and precision. The proposed method has successfully been applied for the simultaneous determination of maneb and zineb in several synthetic samples, spiked water samples and crops.

Keywords: HPSAM, Maneb, Zineb, Simultaneous Determinations and PAN

◆

INTRODUCTION

Pesticides are an integral part of agricultural production. Apart from their importance in helping to increase the world food supply, they safeguard the crop yields which are necessary to guaranty a minimum profitability to the farmer. But pesticides also pose a global environmental pollution problem by contaminating water, soil and food. The major water, soil and food contaminants belong to the family of carbamate and organophosphate pesticides, which are ubiquitously used in agriculture. Pesticides are highly persistent in the environment, thus polluting the water supply and food chains [1]. Dithiocarbamates are synthetic molecules frequently employed in agriculture as pesticides and in the rubber industry as vulcanization accelerators and anti-oxidants. Dithiocarbamate compounds are classified from medium to highly toxic substances, depending on their structure [2]. Maneb [ethylene-bis (dithiocarbamato)] manganese (II) is one of the dithiocarbamate pesticides, used to control late blight of potatoes and anthracnose of tomatoes. Zineb {[ethylene-bis (dithio carbamato)] zinc (II)} is used as fungicide to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport [2].

It is also used to protect fruits and vegetables from foliar diseases. As dithiocarbamate pesticides are known to have toxicological and mutational effects [3], it is necessary to develop a rapid and accurate analytical method for their determination. Common methods for dithiocarbamate determinations are based on their hot acid decomposition, followed by detection of carbon disulfide (CS_2) evolved after its collection in a suitable solution [4-6]. This approach was first proposed by [Clarke et. al.4 and Lowen 5] who employed different methods for CS_2 quantification and these methods are unable to distinguish among various Dithiocarbamates as most of them get decomposed to CS_2. These methods are also time consuming, laborious and require considerable experimental skill for good results.

REVIEW OF LITERATURE

In the past few years, direct determination of Dithiocarbamates (without hot acid decomposition) has also been carried out by UV-visible spectrophotometry [7-10] voltammetry [11, 12] high performance liquid chromatography [13], capillary electrophoresis [14, 15] flame atomic absorption spectrometry [16, 17]. Maneb and zineb have also been determined by converting it into molybdenum [18, 19] and copper complexes [20]. However all of these methods suffer from one or the other disadvantages. With some of these methods sensitivity is low, some demand expensive and complicated instruments some require expensive or toxic reagents and others require difficult and time-consuming separation procedures and none of these methods is suitable for simultaneous determination of both these pesticides. There is no published example of any of the above mentioned methods and H-Point standard addition method (HPSAM) having been employed for simultaneous determination of maneb and zineb. The simultaneous determination of these pesticides by the use of traditional spectrophotometry techniques is difficult as, their absorption spectra overlap and the superimposed curves are not suitable for quantitative evaluation.

In the present work a very simple, sensitive, selective and low cost HPSAM for simultaneous determination of maneb and zineb using 1-(2-pyridylazo)-2-naphthol in Triton X-100 micellar media is described. The method has been successfully applied for simultaneous determination of maneb and zineb in synthetic samples, spiked water samples, crops (potatoes and wheat grains).

For each measurement, about 2mL of the solution was transferred to a spectrophotometer cell and absorbencies were measured at 543 and 569 nm. Synthetic samples containing different amounts of maneb and zineb were prepared, and known amounts of zineb were added and H-point graphs were constructed. The concentration of zineb was evaluated from C_H and that of maneb was evaluated by the calibration method with a single standard and the ordinate value of the H-point (A_H).

RESULTS AND DISCUSSION

Maneb and zineb formed wine red colored complexes with PAN. Figure 1 clearly shows the overlapping absorption spectra of the PAN complexes of maneb and zineb so each compound interferes with the analytical determination of the other. Therefore simultaneous determination of maneb and zineb is possible using binary HPSAM.

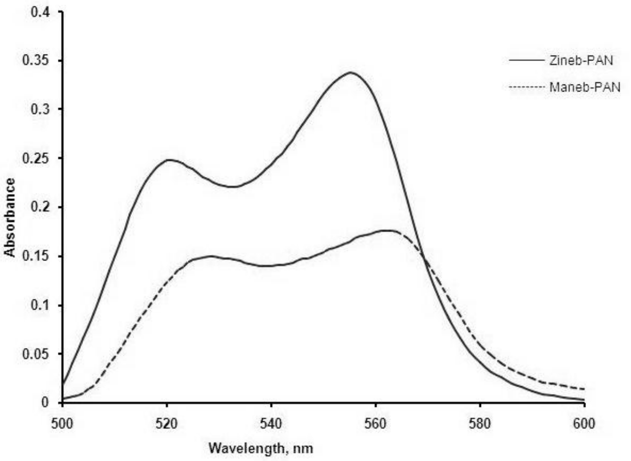

Figure 1- Absorption spectra of 1.326 µg mL^{-1} Maneb-PAN and 1.378 µg mL^{-1} Zineb-PAN complexes at pH 9.2 in micellar media

Optimization of variables

Maneb and zineb form complexes rapidly with PAN at pH values greater than 7. The absorbance is maximum and constant in the pH range 8.0-11.0 for Maneb-PAN, and 9.0- 11.0 for Zineb-PAN complex. Therefore for further studies pH 9.2 was selected. Maneb and zineb-PAN complexes were insoluble in water, but were soluble in micellar media. The effect of various surfactants such as cetylpyridinium bromide (CPB), sodiumlauryl sulfate (SLS), Triton X-100, cetyltrimethylammonium bromide (CTAB) was studied. All these surfactants readily solublize the Maneb-PAN and Zineb-PAN complex but Triton X-100 was preferred as absorbance was maximum and 2.5 mL of 1% Triton X-100 was sufficient for complete dissolution of the each of the complex and for greater amounts the absorbance remained unchanged. Experiments showed that 1.0 mL of (0.01%) PAN solution was optimum for the complete complexation of maneb or zineb.

H-point standard addition method

The spectrum of Maneb-PAN complex was broad so, for obtaining good accuracy, only zineb was considered as analyte. The following principles were followed for selection of appropriate wavelengths for applying HPSAM:

(i) At the two selected wavelengths, the signal of maneb (interferent) must remain same, even if the concentration of zineb (analyte) is changed.

(ii) The analytical signals of the mixture composed from the zineb (analyte) and the maneb (interferent) should be equal to the sum of the individual signals of two species.

(iii) The slope difference of the two straight lines obtained at two selected wavelengths (_1 and _2) must be as large as possible in order to get good accuracy. In this case it is possible to select several pairs of wavelengths with the same absorbance for the Maneb-PAN complex. By considering the criteria that the higher the value for slope increment, the smaller the error for the analyte concentration, the best wavelength pair of 543 and 569 nm were chosen.

Several synthetic samples with different concentration ratios of maneb and zineb were analyzed using HPSAM. The results are given in Table 1. H-point standard addition plots for several synthetic samples are also shown in Figures 2 and 3. It is clear from these Figures that concentration of zineb (CH) is independent of the concentration of maneb, and absorbance proportional to maneb concentration (AH) is also independent of zineb concentration.

Interference analysis

The effect of various diverse ions on the absorbance of a solution containing 0.5 µg mL-1 each of maneb and zineb was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample greater than 5%. Among the anions examined I^-, Br^-, Cl^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, NO_3^-, IO_3^-, NO_2^- - did not interfere at concentrations1000 times higher than those of the analytes but ethylenediamine tetra acetate ion interfered strongly.

Among the cations Hg^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+} and Fe^{3+} were masked with 1.0 mL of 5% sodium fluoride solution. Bi2+, Pb2+ and Th4+ were masked with 2.0 mL of 1 M sodium citrate solution. Other dithiocarbamate pesticides such as dib am (sodium dimethyldithiocarbamate), vapam (sodium monomethyldithiocarbamate), nab am (sodium ethylenebisdithiocarbamate), sodium N-methylanilinecarbodithioate, potassium morph line- 4-carbodithioate did not interfere in the determination of maneb and zineb. Ferbam interfered in the determination of maneb and zineb and was masked with 1.0 mL of 5% sodium fluoride solution.

Table 1- Results of several experiments for the analysis of maneb and zineb in synthetic samples by HPSAM

A-C Equation	r	Present, μgmL^{-1}		Found, μgmL^{-1}		% Recovery	
		Maneb	Zineb	Maneb	Zineb	Maneb	Zineb
$A_{569}=0.4625C_i+0.4665$	0.9993	1.592	0.552	1.585	0.543	99.56	98.36
$A_{543}=0.7931C_i+0.6460$	0.9995						
$A_{569}=0.4639C_i+0.7866$	0.9997	1.592	1.241	1.575	1.234	98.93	99.44
$A_{543}=0.7942C_i+1.1942$	0.9991						
$A_{569}=0.5109C_i+1.0710$	0.9992	1.246	1.792	1.244	1.765	99.84	98.49
$A_{543}=0.7932C_i+1.5693$	0.9995						
$A_{569}=0.5213C_i+1.2195$	0.9997	1.246	2.068	1.223	2.020	98.15	97.67
$A_{543}=0.8069C_i+1.7965$	0.9995						
$A_{569}=0.3649C_i+0.8460$	0.9994	0.716	1.930	0.697	1.962	97.35	99.79
$A_{543}=0.6766C_i+1.3982$	0.9985						
$A_{569}=0.3649C_i+0.8460$	0.9992	1.194	1.930	1.173	1.882	98.24	97.51
$A_{543}=0.6932C_i+1.4637$	0.9996						
$A_{569}=0.3126C_i+0.5287$	0.9998	0.451	1.516	0.445	1.497	98.66	98.75
$A_{543}=0.5926C_i+0.9480$	0.9993						
$A_{569}=0.3205C_i+0.6152$	0.9997	1.008	1.516	0.999	1.495	99.11	98.61
$A_{543}=0.5989C_i+1.0315$	0.9991						

APPLICATIONS OF THE METHOD

Determination of maneb and zineb in water sample

The spiked water samples containing both zineb and maneb have been analyzed by the proposed HPSAM. Maneb and zineb concentration found in water samples by applying HPSAM is in good agreement with the concentration present in the spiked samples actually. The results are given in Table 2.

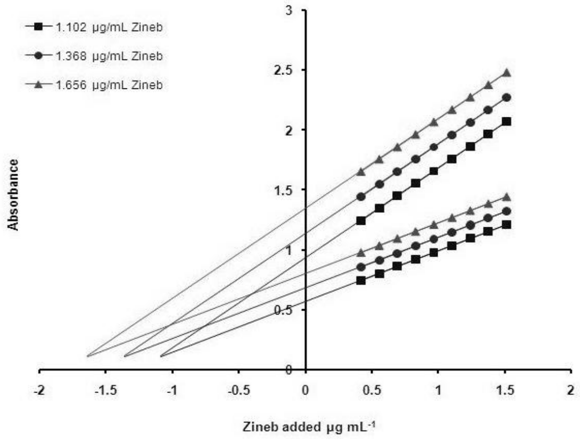

Figure 2- H-point standard addition plots for fixed maneb concentration (0.795 μg mL-1) and different concentrations of zineb

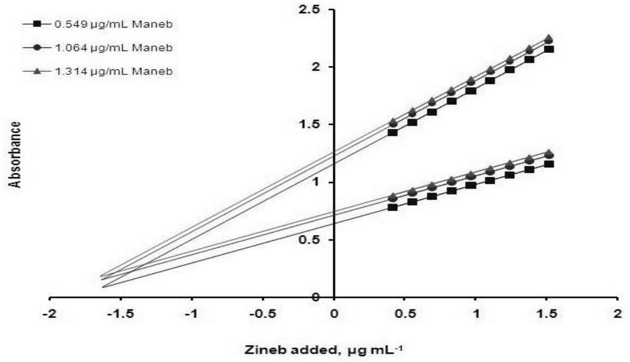

Figure 3- H-point standard addition plots for fixed zineb concentration (1.655 μg mL-1) and different concentrations of maneb

Table 2- Determination of maneb and zineb in different samples by HPSAM

Sample	Concentration, μg mL^{-1}			
	Spiked		Found	
	Maneb	Zineb	Maneb	Zineb
Tap water*	1.687	2.326	1.690	2.331
Tap water**	0.862	1.258	0.867	1.264
Potato	1.780	1.729	1.765	1.733
Wheat	3.223	3.127	3.191	3.129

A known amount of maneb and zineb in DMSO was crushed with 20g of crop. The mixture was then stirred with magnetic stirrer for 1h to provide complete dissolution of maneb and zineb and then filtered to separate the food residue from the solution containing maneb and zineb. The residue was washed with DMSO to provide complete extraction of maneb and zineb to the solution. Filtrate and washings were combined and evaporated to 20mL on a water bath using a current of dry air, dissolved in

DMSO and determined by the HPSAM. The results of the determinations are given in Table 2.

CONCLUSION

The important characteristics of this work are Simultaneous determination of maneb and zineb without the use of any expensive instrument is achieved. This reduces the cost of applied method. And No extraction step is required as determination has been done in micellar media and hence the use of organic solvents is avoided. Most of the organic solvents that are being used for extraction are classified as toxic and environmental pollutants and some have been listed as carcinogenic by the US Environmental Protection Agency (EPA).

REFERENCES

1. Barceló D, Environmental Analysis: Techniques, Applications and Quality Assurance: Elsevier, Amsterdam, 1993.
2. Edwards I R, Ferry D G and Temple W A, Handbook of Pesticide Toxicology: Academic Press, New York, 1991.
3. Committee for Analytical Methods for Residues of Pesticides and Veterinary Products in Foodstuffs of the Ministry of Agriculture, Fisheries and Food, Analyst., 1981,106, 782.
4. Clarke D G, Baum H, Stanley E L and Hester W F, Anal Chem., 1951, 23, 1842.
5. Lowen W K, Anal Chem., 1951, 23, 1846.
6. Hall C H, J Assoc Off Agric Chem., 1960, 43, 371.
7. Kesari R and Gupta V K, Talanta., 1988, 45, 1097.
8. Mathew L, Rao T P, Iyer C S P and Damodaran A D, Talanta, 1995, 42, 41.
9. Malik A K, Kapoor J and Rao A L J, J Environ Monit., 2000, 2, 367.
10. Kapoor J and Rao A L J, Pestic Sci., 1994, 42, 109.
11. Ulakhovich N A, Medyantseva E D, Froleva V F and Romanova O N, Zh Anal Khim., 1983, 38, 1963.
12. Ulakhovich N A, Shaidarova L G, Budnikov G K and Anisimova L A, Zh Anal Khim., 1991, 46, 2398.
13. Gustafsson K H and Fallgren C H, Agric Food Chem., 1983, 31, 461.
14. Malik A K and Faubel F, Fresenius J Anal Chem., 2000, 367, 211.
15. Malik A K and Faubel W, Talanta., 2000, 52, 341.
16. Baena J R, Gallego M and Valcarcel M, Analyst, 2000, 125, 1495.
17. Turker A R and Sezer B, G U Journal of Science., 2005, 18, 93.
18. Verma N and Rao A L J, Rev Roum Chim., 1990, 35, 625.
19. Rao A L J and Verma N, Talanta., 1989, 36, 1041.
20. Rangaswamy J R, Poornima P and Majumder S K, J Assoc off Anal Chem., 1971, 54, 1120.