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Quantification of ziram and zineb residues in fog-water samples

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Abstract

The present paper describes the extractive quantification of zinc-dithiocarbamate fungicides, i.e. ziram (zinc bis-dimethyldithiocarbamate) and zineb (zinc ethylene-1,2-bis-dithiocarbamate) in fog-water samples. The method is based on the releasing of equivalent amount of zinc from the fungicides and its subsequent determination by visible spectrophotometry or by flame-atomic absorption spectrometry (flame-AAS). For spectrophotometry, the sample contained up to 48 μg of ziram and 42 μg of zineb was first equilibrated with chloroform. The recovery results show that only ziram content was extracted into chloroform. Then, the sample was treated with NH_4SCN and surfactants (i.e. CPC and TX-100) solutions, and extracted with toluene to remove interference of inorganic zinc and other metal ions, if present in the sample. The residue was further used for zineb determination. The chloroform extract and residue were then digested separately with nitric acid to release Zn(II), which were then analyzed spectrophotometerically with 4-(2-pyridylazo)-resorcinol in the micellar medium (TX-100) for the determination of ziram and zineb, respectively. The complex shows λ_{max} at 495 nm. The molar absorptivity in terms of ziram/zineb was determined to be $(8.05) \times 10^4$ L mole^{-1} cm^{-1}. The detection limits for ziram and zineb were calculated to be 20 and 21 μg L^{-1} (with R.S.D. $< 1.5\%$), respectively. Whereas, the optimum concentration ranges were 0.08–1.6 and 0.07–1.4 mg L^{-1}, respectively. Alternatively, the Zn contents present in chloroform extract and in residue were directly analyzed using flame-AAS without undergoing the digestion procedure, and ziram and zineb were determined, respectively. The optimum concentration ranges were 0.9–4.8 and 0.8–4.3 mg L^{-1}, while the detection limits were calculated to be 145 and 144 μg L^{-1}, respectively with R.S.D. $< 2.5\%$. The methods are free from interference of almost all ions [including Zn(II)] and other dithiocarbamate pesticides, which can commonly associate with ziram/zineb in fog-water.

Keywords: Ziram and zineb; Separation; Spectrophotometry; Flame-AAS; Fog-water

1. Introduction

Zinc bis-dimethyldithiocarbamate (ziram) and zinc ethylene-1,2-bis-dithiocarbamate (zineb) are well known dithiocarbamate (DTC) fungicides widely used for controlling diseases of fruit and vegetable crops, such as anthracnose, shot-hole, brown rot, early blight, scab, downy mildew, etc. [1,2]. They also used as vulcanization accelerators and antioxidants in the rubber industry [3]. Zinc bis-dimethyldithiocarbamate produces disulfiram (Antabuse) effect on alcohol metabolism [4,5]. Zinc ethylene-1,2-bis-dithiocarbamate metabolites to ethylenethiourea, which is a potent animal carcinogen [4,5]. This metabolite may also account for the antithyroid effects in humans [4,5]. Whereas, carbon disulfide is a common metabolite of all DTC fungicides, which poses more acute poisoning [4,5]. Direct effect of exposure to these fungicides can cause allergy to skin, and inflammation of eyes and respiratory tract in humans [3–5]. Long-term exposure can cause functional changes in the cardiovascular system in humans [3–5]. The reported oral LD_{50} values for ziram and zineb are 1400 and 7600 mg kg^{-1} [3,6,7], respectively for rats. Other than industrial exposures, mostly they contaminate the environment at the time of their agricultural uses. The suspended particles of pesticides in air are then removed by rainfall [8,9]. Their removal with fog droplets is significantly higher due to enhance residence time for diffusion phenomenon, and thus the fungicide accumulates in fog droplets in many folds [10]. Moreover, monitoring of

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the fungicide level in fog-water can also be an efficient way to assess the contamination level in the atmosphere as fog droplets can be a direct source or indirect pathway of fungicides ingestion for human being and other living organisms.

Various instrumental methods have been reported for the determination of DTC fungicides, such as spectrophotometry [11–16], high-performance liquid chromatography-UV (HPLC-UV) [17], atomic absorption spectrometry (AAS) [18], differential pulse-polarography [19], headspace gas-chromatography (GC) [20], liquid chromatography (IC) [21], fourier transform infrared spectrometry (FTIR) [22] etc. Including the standard procedure recommended by the AOAC Official Methods of Analysis [23], most of them are based on the quantification of CS_2, evolved during the acid hydrolysis [11,12,15,20]. Similarly, Agrawal et al. [24] determined zineb spectrophotometrically estimating the evolved H_2S during the acid hydrolysis at room temperature. Recently, Coldwell et al. [25] also reported the determination of dithiocarbamate pesticides using GC, based on CS_2 evolution. The biggest disadvantage of CS_2 dependent methods is the lack of selectivity, since all dithiocarbamate pesticides release CS_2 on acid hydrolysis. Some spectrophotometric methods have been reported for selective determination of a DTC pesticide using prior extraction and digestion based on its elemental analysis [14,26]. Baena et al. [18] also reported an AAS method for determination of metal DTCs prior to sorption by C_{60} fullerene. But speciation of ziram and zineb is a challenging task as both of the fungicides contain zinc. Malik and Faubel [27] suggested capillary electrophoresis separation followed by UV detection of ziram and zineb, but method is less sensitive, and thus inadequate to be applied on samples containing the pesticides in sub ppm levels.

The goal of this study was to develop a quantitative separation procedure of ziram and zineb in fog samples and their simple and sensitive determination. The method has been successfully applied to fog samples collected from agriculture sites.

2. Experimental

2.1. Instrumentation

An UV–vis spectrophotometer, type-106 (Systronics), 1-cm matched quartz cells, and an atomic absorption spectrometer, type-932AA (GBC) equipped with Zn hollow cathode lamp (GBC) were used in this study.

2.2. Reagents

Analytical-grade reagents and deionized, double-distilled water were used throughout the experiment.

Ziram and zineb were obtained from Riedel-de Haen (Germany). Stock solution of ziram was made by dissolving 10 mg in 100 mL of acetonitrile (Merck, Germany). The zineb solution was prepared by dissolving 10 mg in 100 mL of dimethylsulfoxide (Merck, Germany). The working standards were prepared by appropriate dilution of the stock solutions.

Working solution of PAR was freshly prepared by dissolving 45 mg of 4-(2-pyridylazo)-resorcinol (TCI, Japan) in 100 mL of ethanol (Merck, Germany).

Borate buffer solution (pH 8.7 ± 0.02) was prepared by mixing H_3BO_3 (Merck, Germany) and KCl (Merck, Germany) (100 mL each, 0.2 M) and adjusting the pH to 8.7 ± 0.02 using 0.2 M NaOH (Merck, Germany).

A 2 M ammonium thiocyanate (BDH, India) solution (15%, w/v) was freshly prepared.

A 5.0×10^{-3} M polyoxyethylene-*p*-tert-octylphenol (TX-100) (Lancaster, England) and a 1.3×10^{-2} M cetylpyridinium chloride (CPC) (Acros Organics, USA) solutions were used.

2.3. Fog sampling

The fog-water samples were collected on event basis in night (18:00–6:00 h) during late November 2001 to January 2002. The standard fog collectors (SFCs), proposed by Schemenauer and Cereceda [28] designed with the 35% shade coefficient polypropylene mesh of double layer (supplied by Tiddenet Ltd., UK) fixed on a 1 m^2 aluminium frame (diameter, 1 cm), 2 m above from ground on a stand, was employed. Below the net, a polyethylene trough (10 cm × 15 cm × 1 m) connected with an outlet tube, was placed to collect over night fog deposited into a 250-mL borocil measuring cylinder. The SFCs were hosted in between or near by the farms of wheat, tomato and potato within two days of the pesticides applications. The agriculture farms are located near by Raipur city (21°14′ N latitudes, and 81°38′ E longitudes at altitude >300 m) of central India. The collected samples were filtered (through Whatmann filter no. 42) into 250-mL polyethylene bottles, packed in iceboxes and brought to the laboratory. All samples were refrigerated at 4 °C for analysis and were analyzed within 48 h from their collection time.

2.4. Method for determination

2.4.1. Separation of ziram and zineb present in a sample

An aliquot of sample solution containing ziram and zineb within optimum concentration ranges of the methods was taken in a 125-mL separatory funnel and was equilibrated with 10 mL of chloroform for 1 min. The chloroform extract (A) was collected in a 50-mL beaker, whereas the residue was again treated with 1 mL NH_4SCN, 0.2 mL CPC and 0.1 mL TX-100, and was extracted with 10 mL of toluene for 1 min. The toluene extract was discarded and the residue (B) was used for zineb determination. The chloroform extract and residue were then directly employed for flame-AAS determination of the fungicides or, for spectrophotometric determination, evaporated separately to 1 mL on a water bath

in a hood and wearing mask. After cooling at room temperature, 1 mL concentrated nitric acid was added to each of the residues. The solutions were again evaporated to just before the drying condition. After few minutes, 5 mL water was added to each, and warmed the solutions at 50–60 °C for 2–3 min. These solutions (A → A1 and B → B1) were filtered through Whatmann filter no. 42 into 30-mL volumetric flasks by washing thrice with about 4 mL of warmed water, and proceeded further for analysis.

2.4.2. Spectrophotometric determination

After cooling at room temperature, 6 mL borate buffer (pH 8.07 ± 0.02), 3 mL PAR solution and 1.5 mL TX-100 solution were added to each of the solutions (A1 and B1) and diluted to the mark by adding water and homogenized by shaking. The absorbance of the solutions was measured at 495 nm against the reagent blanks prepared in the same way. The concentration of ziram/zineb was calculated using calibration graph, which was prepared by measuring absorbance with a series of standard solutions treated in the same way as sample solutions.

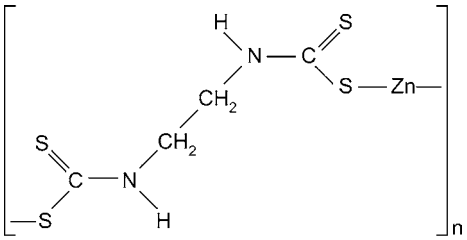
2.4.3. Flame-AAS determination

The instrument was set through the operating software under the recommended conditions, i.e. wavelength = 213.9 nm, lamp current = 5 mA, slit width = 0.5 nm, flame = air–acetylene (2.5/8, v/v). Prior to the chloroform extract (A) and the residue (B) of the sample solution injection, the series of standard solutions prepared in the same way were injected into flame-burner of AAS one by one for calculating the calibration data, and the concentration of the ziram and zineb in sample solution was noted, respectively.

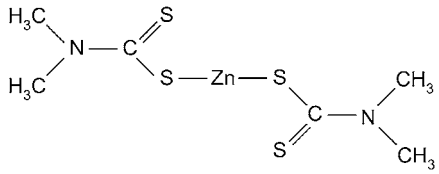
3. Results and discussions

3.1. Quantification of ziram and zineb

Quantification of dithiocarbamate pesticides based on acid hydrolysis with the measurements of the released carbon disulfide or metal ion can only be specific if separation of dithiocarbamates is possible. In this study, it was observed that only ziram was extracted into chloroform if both of the fungicides are present in very low concentration (ppm level). This is because of their structural dissimilarities. Zinc bis(dimethyldithiocarbamate) has monomeric structure whereas, zinc ethylene bis(dithiocarbamate) has polymeric structure (Fig. 1), which makes zineb to be insoluble in common organic solvents like chloroform [29,30], and thus this characteristic is used for their separation in this work. The separation was carried out by taking a known volume of ziram and zineb solutions in a 125-mL flask, and the percentage extractions (recoveries) were performed at different pH values, 3.1–9.2 (varying by adding few drops of NH_4OH or CH_3COOH solutions**)** after the digestion of the extractants followed by the determinations (spectrophotometrically) as described in the procedure. The results show that chloroform was found to extract 98.7 ± 0.6% ($n = 21$) of 0.8–1.6 mg L^{-1} ziram, in presence of 1.4 mg L^{-1} zineb at pH ≤ 7.9 of the sample solution. The percentage extraction shows positive biased over pH 8 of the sample solution,



A. [zinc ethylene bis(dithiocarbamate)/zineb]



B. [zinc bis(dimethyldithiocarbamate)/ziram]

Fig. 1. Structure of: (A) ziram; and (B) zineb.

Table 1
Recovery results of extraction of ziram at different pH

pH for extraction	Ziram added (μg), in presence of 28 μg zineb	Ziram found[a] (recovery, %)	R.S.D.[b] (%)	Zineb found[a] (recovery, %)	R.S.D.[b] (%)
3.1, 3.3, 3.0	16, 28, 32	98.5, 97.7, 98.4	1.2, 1.0, 0.8	98.5	1.1
4.2, 4.3, 4.4	17, 25, 31	99.3, 97.8, 98.8	0.9, 1.3, 1.3	98.9	1.3
5.0, 5.3, 5.1	17, 26, 32	98.5, 98.0, 98.4	1.0, 1.0, 1.1	99.0	0.8
5.7, 5.8, 5.9	18, 27, 31	97.9, 98.7, 99.1	0.9, 0.8, 0.7	99.5	1.0
6.5, 6.3, 6.4	16, 24, 30	99.5, 98.7, 98.8	0.6, 0.7, 1.1	98.8	1.2
7.2, 7.1, 7.3	19, 27, 32	98.6, 99.2, 99.0	1.2, 0.9, 0.7	98.1	0.9
7.8, 7.9, 7.7	17, 24, 31	100.1, 99.7, 98.7	0.9, 0.8, 1.0	98.1	1.5
8.1, 8.3, 8.2	16, 24, 30	99.9, 100.8, 100.2	0.6, 1.1, 1.0	97.9	0.9
9.0, 9.1, 9.2	16, 26, 32	101.8, 100.4, 101.1	0.7, 1.0, 0.9	97.5	1.0

[a] Average of four replicate measurements.
[b] Based on four replicate measurements.

might be due to partial extraction of zineb into chloroform (Table 1).

The effect of dilution, i.e. ratio of organic phase to that of aqueous phase was also studied on the extraction of 0.08 and 1.6 mg L^{-1} ziram in presence of 0.07 and 1.4 mg L^{-1} zineb in each of the case, and steady readings were obtained in the ratio (volume-organic: volume-aqueous) ranged from 1:1 to 1:5. However, the upper limit can be increased by increasing the shaking time. For the said ratios, 1 min of shaking duration was found to be sufficient. A 15–30 °C temperature range was found to be adequate for the extraction (all the extractions were carried-out at room temperature, 22 ± 2 °C). After removal of chloroform layer remaining sample was used for zineb determination**.** The results show that >98% of ziram and zineb were recovered with <1.5% R.S.D. Optimization of other parameters/conditions of digestion (nitric acid process) was also been studied and their optimal values were adopted.

The interference of inorganic zinc, other metal ions in the remaining sample was overcome by extracting them into toluene as metal-thiocyanato complex in the presence of surfactants. The presence of surfactants made the complex to be extractable into organic solvents [31]. The percentage extractions of the metal ions [Fe(III), Co(II), Mn(II), Cu(II), Zn(II)] in different solvents (chloroform, toluene, benzene, MIBK) were performed at pH 4–8, and among them toluene was found to be most suitable solvent for all metal ions with percentage extractions >97% (R.S.D. < 2.5%). The concentration effect was studied and optimum concentrations of ammonium thiocyanate and surfactants were used.

3.2. Determination of ziram and zineb

Zinc(II) forms binary chelate complex with 4-(-2-pyridylazo)-resorcinol, which is reported widely for the determination of Zn(II) [32]. The absorption spectra of Zn(II)-PAR complex was measured against the reagent blank prepared under similar conditions. The complex shows maximum absorbance at 495 nm. The maximum sensitivity was observed over pH range from 7.7 to 10.2. For the selective determination of Zn the pH was kept 8.7 ± 0.02 throughout the work. The effect of different surfactants, such as cationic [cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide (CTAB)], nonionic [polyoxyethylene(23)lauryl ether (Brij-35), TritonX-100(TX-100)] and anionic [sodium lauryl sulfate (SLS)] on the molar absorptivity was studied. The molar absorptivity was decreased slightly in the presence of anionic or cationic surfactants with the shifting of λ_{max} to +5 or +10 nm, respectively. Whereas, the sensitivity of the method was found to be increased in the presence of the nonionic surfactant, TX-100 without affecting the λ_{max} [33].

The mole ratio of Zn^{2+} to PAR^{2-} and TX-100 was determined by the curve fitting method, plotting log (A_{equ}/A_{max}-A_{equ}) versus log (molar concentration of the reagent solution taken), and Zn^{2+} to PAR^{2-} was found to

Table 2
Results of ziram and zineb analysis in fog samples

Sample no.	Sampling date	Farm area about (acre)	Sprayed concentration of ziram/zineb (ub/100 gu/acre)	Fungicide applied before the sampling started (h)	Sample volume (mL)	By spectrophotometer				By flame-AAS			
						Ziram found		Zineb found		Ziram found		Zineb found	
					s	μg L^{-1}	R.S.D.[a] (%)	μg L^{-1}	R.S.D.[a] (%)	μg L^{-1}	R.S.D.[a] (%)	μg L^{-1}	R.S.D.[a] (%)
#1	Nov 25'01	12	1.5/1.5	10	50	404	1.1	231	0.8	420	2.6	221	1.8
#2	Dec 8'01	10	2.0/–	22	56	213	0.9	ND		219	1.9	ND	
#3	Dec 15'01	6	1.5/1.0	36	58	149	1.0	112	0.9	151	2.0	122	2.1
#4	Dec 22'01	8	1.5/1.0	10	65	326	0.7	215	1.1	342	2.4	207	1.7
#5	Jan 05'02	6	1.5/1.0	22	75	178	0.8	105	1.2	185	2.0	104	1.7
#6	Jan 10'02	8	–/1.5	10	82	ND		167	1.0	ND		161	2.0
#7	Jan 17'02	5	1.5/1.5	40	74	98	0.8	58	0.9	88	1.9	61	1.7
#8	Jan 21'02	4	–/2.0	10	68	ND		187	1.2	ND		180	1.9

[a] Four replicate measurements were taken; ND: not detected; –: not applied.

be 1:2, while Zn(II) to TX-100 could not be determined precisely. Thus, the probable reaction mechanism can be expressed as:

$$Zn^{2+} + 2PAR^{2-} + mTX\text{-}100 \Leftrightarrow [Zn(PAR)_2]^{2-}mTX\text{-}100 + 4H^{+}$$

where, m denotes the number of TX-100 molecules. The non-ionic surfactant, increases the solubility of the complex results in the enhancement of the absorptivity as described by Liu and Chang [34]. In this work at least 2.5×10^{-4} M TX-100 was needed to get the maximum absorbance and its further addition up to 4.0×10^{-4} M, had no adverse effect on the absorbance. Its addition beyond this limit caused the solution to be turbid.

3.3. Interference

Like Zn(II) several metals ions such as Cu(II), Ni(II), Co(II), Fe(III), Al(III), Mn(II) etc. were reported to form complex with PAR. However, the pH range, λ_{max}, etc. are different for most of the ions, or some of the ions can be masked for the selective determination of Zn. A known amount of different ions which can form complexes with PAR such as Zn(II), Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Al(III), Mn(II) etc. were used in order to verify procedure selectivity. In the extraction/determination of ziram, all of the species did not interfere, even when they were present more than 100-fold excess because none of them was found to be extracted with chloroform. Interference of some other DTC pesticides like ferbam, cufraneb, cuprobam, maneb etc. was masked by adjusting pH and adding some masking agents e.g. formation of Fe(III)-PAR complex and Cu(II)-PAR complex is hindered at pH higher than 8 [35]. Maneb was masked by adding few drops of 0.001 M nitriloacetic acid (NTA). In the case of zineb determination, Zn(II), Cu(II), Co(II), Fe(III), etc. present in the sample were removed as thiocyanate-surfactant complex and extracted with toluene before the digestion process. Whereas, Ni(II) was masked by adding citrate and Al(III), Mn(II) by adding few drops of 0.001 M nitriloacetic acid (NTA) [36].

3.4. Analytical figures of merit

For the spectrophotometry, the molar absorptivity was found to be $(8.05) \times 10^4$ L mole^{-1} cm^{-1} in terms of ziram/zineb. Calibrations graphs for the determination of ziram and zineb were obtained as described in the procedures, and were linear in the range of 2.4–48 and 2.1–42 μg, respectively. For ziram, the calibration equation was $A = 0.259$ (mg L^{-1} ziram) $+ 4.35 \times 10^{-3}$, where A is the absorbance with a linear range of 0.08–1.6 mg L^{-1} and $r^2 = 0.999$. The 3σ detection limit was calculated to be 20 μg L^{-1} for the level of 0.5 mg L^{-1} ziram with R.S.D. = 1.4%. While for zineb, the calibration equation was $A = 0.291$ (mg L^{-1} zineb) $+ 1.18 \times 10^{-2}$ with a linear range

Table 3
Recovery results

Sample no.	Fog sample taken (mL)	Ziram spiked (μg)	Zineb spiked (μg)	By spectrophotometer						By flame-AAS					
				Ziram found			Zineb found			Ziram found			Zineb found		
				μg	R.S.D.[a] (%)	Rec.[b] (%)	μg	R.S.D.[a] (%)	Rec.[b] (%)	μg	R.S.D.[a] (%)	Rec.[b] (%)	μg	R.S.D.[a] (%)	Rec.[b] (%)
#1	20	10.0	10.0	17.84	0.8	98.7	14.49	0.9	99.1	18.07	2.5	98.2	14.49	2.1	100.5
#3	20	2.0	2.0	4.84	1.1	97.1	4.18	0.8	98.6	4.96	1.9	98.8	4.36	1.7	98.1
#4	20	3.0	5.0	9.38	1.0	98.5	9.13		98.2	9.75	2.1	99.1	9.04	2.0	98.9
#7	20	2.0	2.0	3.86	1.4	97.5	3.07	1.2	97.2	3.68	1.9	97.9	3.16	1.8	98.1

[a] Four replicate measurements were taken.
[b] Recovery calculated based on [(ziram or zineb found)/(present in fog sample, which is calculated from Table 2 + amount spiked)] × 100.

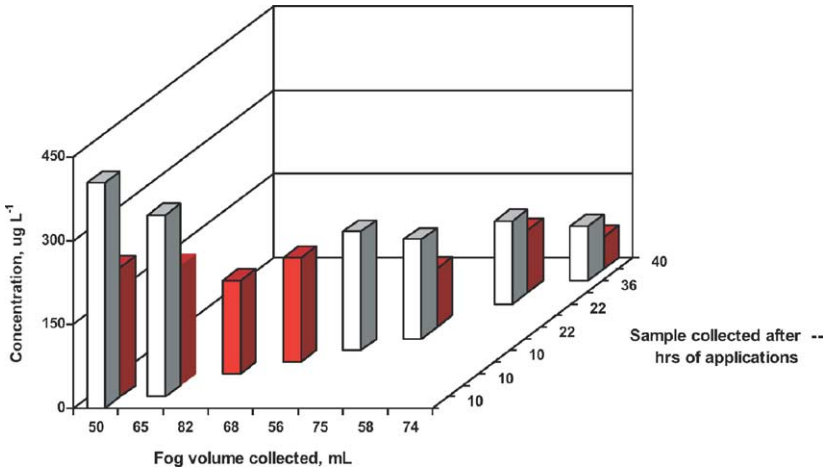


Fig. 2. Effect of fog volume and the time interval from the application on concentration of the fungicides (front bars (hollow) are for ziram and back bars (dark) for zineb).

of 0.07–1.4 mg L^{-1} and $r^2 = 0.999$. Similarly, the detection limit was determined to be 21 μg L^{-1} for the level of 0.5 mg L^{-1} zineb (R.S.D. = 1.4%).

For the flame-AAS determination of ziram and zineb, the calibration equations were $A = 0.306$ (mg L^{-1} ziram)-2.95×10^{-2} (A is the absorbance with a linear range of 0.9–4.8 mg L^{-1} and $r^2 = 0.993$) and $A = 0.327$ (mg L^{-1} zineb)-2.41×10^{-2} (A is the absorbance with a linear range of 0.8–4.3 mg L^{-1} and $r^2 = 0.994$), respectively. The detection limit (3σ) for ziram was found to be 145 μg L^{-1} for 2.0 mg L^{-1} with R.S.D. = 2.4%, whereas for zineb was 144 μg L^{-1} (2.5 mg L^{-1} level with R.S.D. = 2.0%).

3.5. Analysis of fog samples

Fog-water samples were collected on event basis and analyzed as described in the procedures, Table 2. Samples #1 and #2 were collected from near by wheat farms, #3–#6 from tomato farms, #7 and #8 from potato farms. The sprayed concentration for ziram and zineb was in between 1–2 pounds/100 gallon of water/acre area. However, the specific meteorological data on the field are not available for the sampling period but according to the government department, which is located around about 10 km radius distances of the sites, the data during the application and sampling period were: temperature min. = 13 and max. = 31 °C, wind direction = random, wind velocity = 2.5 to 8 km h^{-1}. Thus in general, the data show that with the increase in sample volume and duration between application of the fungicides and sample collection, the concentration of ziram/zineb decreases (Fig. 2).

3.6. Validation of the method

To check the validity and reliability of the present method, a known amount of ziram and zineb was spiked to the fog samples #1, #3, #4 and #7, and analyzed as described in the procedure. The results show that >97% ziram and zineb were recovered with concentration ranged 3–18 μg (Table 3). Furthermore, the data obtained from spectrophotometer and flame-AAS were compared very well with $r^2 > 0.9$.

4. Conclusion

The present method describes the extractive procedure to quantify the Zn-DTC fungicides, which is very useful to estimate the individual impacts of these fungicides as the toxicity differs with the compound. On comparison, it is found that the present method can be applied to quantify ziram and zineb present in a sample, which is not possible with CS_2/H_2S evolve dependent several methods [11,12,15,20,23–25], and also by AAS method [18]. In addition, the method is highly sensitive and simple than CS_2 evolve dependent methods, as handling of CS_2 is crucial and needs perfection. The interference studies show that the method is highly selective as zinc, other ions and other pesticides, commonly found in fog-water did not interfere. The present method provides two options of determination, either by spectrophotometer or by flame-AAS. The selectivity, sensitivity and simplicity of this method make it useful for the routine analysis of the fungicide, and for low budgeted laboratories too.

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