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Method no.: PV2073

Matrix: Air

Target Concentration: 0.4 mg/m<sup>3</sup> (arbitrary). There is no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for ziram.

Procedure: Samples are collected by drawing known volumes of air through OSHA versatile sampler (OVS-2) tubes, each containing a glass fiber filter and two sections of XAD-2 adsorbent. Samples are desorbed with chloroform and analyzed by high performance chromatography (HPLC) using an ultraviolet detector (UV).

Recommended air volume and sampling rate: 180 L at 1.0 L/min

Detection limit of the overall procedure (based on the recommended air volume and the analytical detection limit): 0.01 mg/m<sup>3</sup>

Status of method: Stopgap method. This method has been partially evaluated and is presented for information and trial use only.

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Chemist: Duane Lee

Carcinogen And Pesticide Branch  
OSHA Analytical Laboratory  
Salt Lake City, Utah

## 1. General Discussion

### 1.1 Background

#### 1.1.1 History of procedure

The OSHA Analytical Laboratory received a set of samples requesting the analysis of ziram. The samples had been collected on OVS-2 tubes. This report describes the analytical method developed for ziram.

#### 1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

The oral LD<sub>50</sub> of ziram is 150 mg/kg in guinea pigs, 480 mg/kg in mice, 1400 mg/kg in rats, and 400 mg/kg in rabbits. The intraperitoneal LD<sub>50</sub> of ziram is 73 mg/kg in mice, 23 mg/kg in rats and 50 mg/kg in rabbits. Studies have been done on mice and rats to determine the carcinogenicity of ziram. The data available is inadequate to make a determination. (Ref. 5.1 and 5.2)

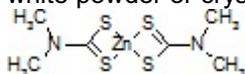
#### 1.1.3 Potential workplace exposure

Ziram is used in various applications. One application found ziram to be useful as a fungicide in 1944. It is registered in the U.S. for use on 24 fruits, vegetable crops and ornamental flowers. Another application of ziram is as an accelerator or promoter in the rubber-processing industry. Also, small amounts of ziram are used in industrial fungicides in combination with 2-mercaptobenzothiazole. In 1973, ziram was produced in the U.S. by eight companies whose combined production amounted to 1 million kg. No estimate of worker exposure could be found. (Ref 5.1)

#### 1.1.4 Physical properties (Ref. 5.1 to 5.4)

CAS number: 137-30-4  
IMIS number: Z126  
Molecular weight: 305.81  
Molecular formula: C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>S<sub>4</sub>Zn  
Melting point: 250 °C (crystals); 148 °C (dust)  
Solubility: Practically insoluble in water; soluble at 0.2 g or less per 100 mL for carbon tetrachloride, diethyl ether and ethanol; soluble at 0.5 g or less per 100 mL for benzene, acetone, naphtha and other non-polar solvents; soluble in chloroform  
Chemical name: Bis(dimethyldithiocarbamato)zinc  
Synonyms: Bis(dimethyldithiocarbamato-S,S')zinc; Antene; Carbazinc; Corset; Human; Drupina 90; Fuclasin; Ultra; Fuklasin; Fungostop; Hexazir; Mezene; Tricarbamix; Triscabol; Zerlate; Zincmate; Ziram Technical; Ziramvis; Zirasan 90; Zirberk; Zirex 90.  
Description: white powder or crystals

Structure:



## UV Scan:

### 1.2 Limit defining parameters

The detection limit of the analytical procedure is 2.1 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

## 2. Sampling Procedure

### 2.1 Apparatus

2.1.1 A personal sampling pump that can be calibrated to within  $\pm 5\%$  of the recommended flow rate with the sampling device in line.

2.1.2 OVS-2 tubes, which are specially made 13 mm o.d. glass tubes that are tapered to 6 mm o.d., packed with a 140-mg backup section, a 270-mg sampling section of cleaned XAD-2 adsorbent and a 13 mm diameter glass fiber filter. The backup section is retained by two foam plugs and the sampling section is between one foam plug and the glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer.

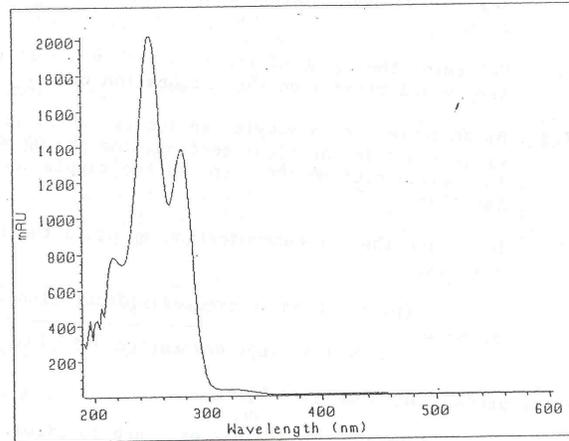


Figure 1.  
UV Scan of Ziram in Mobile Phase

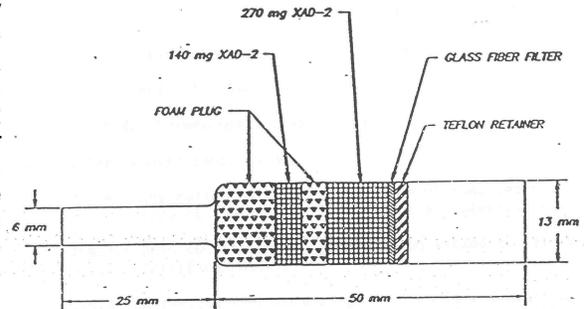


Figure 2.  
OVS-2 Sampling Tube

### 2.2 Reagents

No sampling reagents are required.

### 2.3 Sampling technique

- 2.3.1 Immediately before sampling, remove the plastic caps from the OVS-2 tube.
- 2.3.2 Attach the small end of the tube to the sampling pump with flexible tubing.
- 2.3.3 Attach the tube vertically in the employee's breathing zone in such a manner that it does not impede work performance.
- 2.3.4 After sampling for the appropriate time, remove the tube and seal with plastic caps.
- 2.3.5 Wrap each sample end-to-end with an OSHA seal (Form 21).
- 2.3.6 Record the air volume for each sample, and list any possible interferences.
- 2.3.7 Submit at least one blank for each set of samples. Handle the blank in the same manner as the samples, except no air is drawn through it.
- 2.3.8 Submit bulk samples for analysis in a separate container. Do not ship with air samples.

### 2.4 Desorption efficiency (glass fiber filter and XAD-2 adsorbent)

Six vials each containing a 13-mm glass fiber filter and 270-mg of XAD-2 adsorbent were each liquid spiked on the glass fiber filter with 18  $\mu\text{L}$  of a 4.05 mg/mL solution of ziram. These samples were allowed to equilibrate overnight in a drawer at ambient temperature. The next day each sample was

desorbed with 2.0 mL of chloroform, shaken for 30 min and analyzed as in Section 3. The results are listed in Table 2.4.

## 2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 18  $\mu$ L of a 4.05 mg/mL solution of ziram by spiking the glass fiber filter. These were allowed to equilibrate overnight in a drawer at ambient temperature. The next day 180 L of humid air (~80% relative humidity) were drawn through each tube at 1 L/min. Six of the tubes were each desorbed with 2.0 mL of chloroform, shaken for 30 min and then analyzed as in Section 3. The results are listed in Table 2.5. No ziram was found on the backup sections of these tubes. The remaining samples were stored, six in a drawer at ambient temperature and six in a freezer, for use in the storage study below.

## 2.6 Sample storage

After nine days of storage, the 12 tubes, were each desorbed with 2.0 mL of chloroform, shaken for 30 min and then analyzed as in Section 3. The results are given in Tables 2.6.1 and 2.6.2.

## 2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 180 L.

2.7.2 The recommended flow rate is 1.0 L/min.

## 2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of ziram. Any suspected interferences should be reported to the laboratory.

## 2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

# 3. Analytical Procedure

## 3.1 Apparatus

3.1.1 A balance capable of weighing to the nearest tenth of a milligram. A Mettler HL52 balance was used in this evaluation.

3.1.2 A mechanical shaker.

3.1.3 An HPLC equipped with a UV detector. A Hewlett Packard (HP) 1090M equipped with an autosampler and diode array detector was used in this evaluation.

3.1.4 An HPLC column capable of separating ziram from any interferences. A 50 mm x 4.6 mm i.d. ECON C8 (3  $\mu$ m) liquid chromatography column was used in this evaluation.

3.1.5 An electronic integrator, or some other suitable means for measuring detector response. The Hewlett-Packard 1090M Data System was used in this evaluation.

3.1.6 Volumetric flasks and pipets.

3.1.7 Vials, 2-mL and 4-mL.

## 3.2 Reagents

3.2.1 Chloroform, reagent grade. This was obtained from Burdick and Jackson for this evaluation.

3.2.2 Ziram, reagent grade. A standard obtained from EPA (EPA # 7100, 98% purity) was used in this evaluation.

- 3.2.3 Methanol, reagent grade. This was obtained from Burdick and Jackson for this evaluation.
- 3.2.4 Water, HPLC grade.
- 3.2.5 Zinc sulfate heptahydrate ( $\text{ZnSO}_4 \bullet 7\text{H}_2\text{O}$ ) reagent grade. This was obtained from Mallinckrodt for this evaluation.
- 3.2.6 4-Dodecyldiethylenetriamine, reagent grade. This was obtained from Eastman Kodak for this evaluation.
- 3.2.7 Ammonium acetate, HPLC grade. This was obtained from Fisher Scientific for this evaluation.
- 3.2.8 Zinc chelate (10 mM) of the  $\text{C}_{12}$ -dien-Zn (II) metal chelate. This was prepared by placing 2.71 grams of 4-dodecyldiethylenetriamine and 2.87 grams of  $\text{ZnSO}_4 \bullet 7\text{H}_2\text{O}$  in a liter flask and diluting to volume with water.

### 3.3 Standard preparation

Prepare ziram stock standards by weighing 10 to 15 mg of ziram. Transfer the ziram to separate 10-mL volumetric flasks, and add chloroform to the mark. Make working range standards of 1.0 to 105  $\mu\text{g}/\text{mL}$  by pipet dilutions of the stock standards with chloroform. Store stock and dilute standards in a freezer.

### 3.4 Sample preparation

- 3.4.1 Transfer the 13-mm glass fiber filter and the 270-mg sampling section of the tube to a 4-mL vial. Place the first foam plug and the 140-mg section in a separate 4-mL vial. A small glass funnel can be used to facilitate the transfer of the adsorbent. Discard the rear foam plug. Do not discard the glass sampling tube; it can be reused.
- 3.4.2 Add 2.0 mL of chloroform to each vial and seal with a Teflon-lined cap.
- 3.4.3 Shake the vials for 30 minutes on a mechanical shaker.
- 3.4.4 Transfer, if necessary, the samples to 2-mL vials for use on an HP autosampler.

### 3.5 Analysis

#### 3.5.1 Instrument conditions

Column:	50 mm $\times$ 4.6 mm ECON C8 (3 $\mu\text{m}$ )
Mobile phase:	86% methanol 14% water with 1 mM zinc chelate and 0.13 M ammonium acetate (Ref. 5.5)
Flow rate:	0.5 mL/min
Retention time:	2.54 min
Injection volume:	2.0 $\mu\text{L}$

#### 3.5.2 Chromatogram

### 3.6 Interferences (analytical)

- 3.6.1 Any collected compound having a similar retention time to that of the analyte is a potential interference.
- 3.6.2 HPLC conditions may generally be varied to circumvent interferences.
- 3.6.3 Retention time on a single column is not proof of chemical identity. Analysis on an alternate HPLC column and confirmation by mass spectrometry are additional means of identification.

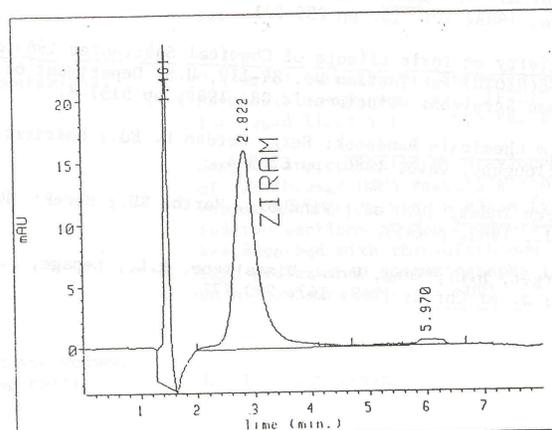


Figure 3.  
Chromatogram of Ziram

### 3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus concentration ( $\mu\text{g}/\text{mL}$ ) of ziram.

3.7.2 Determine the  $\mu\text{g}/\text{mL}$  of ziram in both sections of each sample and blank from the calibration curve.

3.7.3 Blank correct each sample section by subtracting the  $\mu\text{g}/\text{mL}$  found in the blank section from the  $\mu\text{g}/\text{mL}$  found in the sample section and then add the sample sections together.

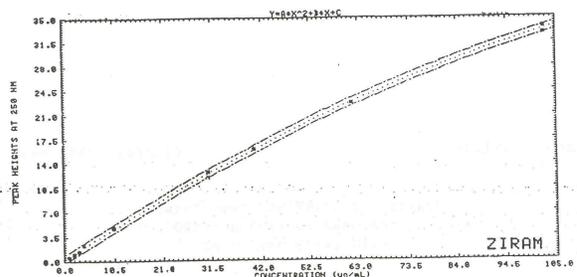


Figure 4.  
Calibration Curve

3.7.4 Determine the air concentration by using the following formula.

$$\text{mg}/\text{m}^3 = \frac{(\text{mg}/\text{mL, blank corrected})(\text{desorption volume, mL})}{(\text{air volume, L})(\text{desorption efficiency, decimal})}$$

### 3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to ziram.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

## 4. Recommendation for Further Study

This method should be fully validated.

## 5. References

- 5.1 IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans; International Agency for Research on Cancer: Lyon, 1983; Vol. 12, pp 259-271.
- 5.2 Registry of Toxic Effects of Chemical Substances 1985-86 Edition; DHHS(NIOSH) Publication No. 87-114, U.S. Department of Health and Human Services: Cincinnati, OH, 1987; pp 5137-8.
- 5.3 Farm Chemicals Handbook; Berg, Gordon L. Ed.; Meister: Willoughby, Ohio, 1986; pp C253-4.
- 5.4 Merck Index, 10th ed.; Windholz, Martha ED.; Merck: Rahway, N.J., 1983; p 1459.
- 5.5 Karger, B.L.; Wong, W.S.; Viavattene, R.L.; Lepage, J.N.; Davies, G. Journal of Chromatography 1968, 167, 253-272.