Method no.:	PV2065
Matrix:	Air
Target Concentration:	0.4 mg/m³ (arbitrary). There is no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for butyl 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):	0.026 mg/m³
Status of method:	Stopgap method. This method has been partially evaluated and is presented for information and trial use only.

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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 butyl ziram. The samples had been collected on OVS-2 tubes. This report describes the analytical method developed for butyl ziram.

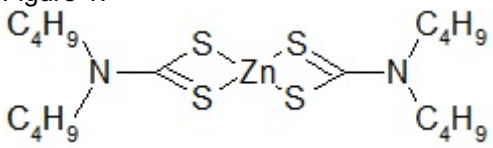
1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

From tumorigenic data on mice, the oral TDLo and the subcutaneous TDLo are 290 gm/kg/78W-1 and 1000 mg/kg respectively. These levels produce tumors in the lungs, thorax, liver and blood. (Ref. 5.2)

1.1.3 Potential workplace exposure

Butyl ziram is used as an accelerator for latex dispersions and cements as well as an ultra-accelerator for lubricating oil additives. No information was available on the number of workers exposed to butyl ziram. (Ref. 5.1)

1.1.4 Physical properties (Ref. 5.1 - 5.2)

CAS number:	136-23-2
IMIS number:	Z129
Molecular weight:	476.19
Molecular formula:	$C_{18}H_{36}N_2S_4Zn$
Melting point:	104-108°C
Specific gravity:	1.24 (20/20°C)
Solubility:	soluble in carbon disulfide, benzene and chloroform; insoluble in water
Chemical name:	Bis(dibutyldithiocarbamato)zinc
Synonyms:	Zinc dibutyldithiocarbamate; Butazate; Carbamic acid, dibutyldithio-, zinc complex; Butyl ziram; Zinc N,N-dibutyldithiocarbamate; Butyl zimate; Vulcacure; Vulkacit LD8/C
Description:	white powder
UV Scan:	Figure 1.
Structure:	

1.2 Limit defining parameters

The detection limit of the analytical procedure is 4.7 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 ± 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 2.)

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 16 µL of a 4.453 mg/mL solution of butyl 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.

Table 2.4
Desorption Efficiency

Sample #	Amount Spiked, µg	Amount Found, µg	% Recovered
Ex1	71.25	71.44	100.3
Ex2	71.25	70.53	99.0
Ex3	71.25	71.61	100.5
Ex4	71.25	72.02	101.1
Ex5	71.25	71.21	99.9
Ex6	71.25	72.04	101.1
		Average	100.3

2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 16 µL of a 4.453 mg/mL solution of butyl 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 butyl 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.

Table 2.5
Retention Efficiency

Sample #	Amount Spiked, µg	Amount Found, µg	% Recovered
Ex1	71.25	70.12	98.4
Ex2	71.25	69.99	98.2
Ex3	71.25	66.35	93.1
Ex4	71.25	65.79	92.3
Ex5	71.25	69.10	97.0
Ex6	71.25	67.35	94.5
		Average	95.6

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.

Table 2.6.1
Ambient Storage

Days Stored	Amount Spiked, µg	Amount Found, µg	% Recovered
9	71.25	65.69	92.2
9	71.25	60.77	85.3
9	71.25	62.07	87.1
9	71.25	58.70	82.4
9	71.25	60.26	84.6
9	71.25	62.89	88.3
		Average	86.7

Table 2.6.2
Freezer storage

Sample #	Amount Spiked, µg	Amount Found, µg	% Recovered
9	71.25	63.85	89.6
9	71.25	58.00	81.4
9	71.25	66.25	93.0
9	71.25	60.98	85.6
9	71.25	63.06	88.5
9	71.25	62.21	87.3
		Average	87.6

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 butyl 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 butyl ziram from any interferences. A 50 mm x 4.6 mm i.d. ECON C8 (3 µm) 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 Butyl ziram, reagent grade. A standard obtained from H.M. Royal Incorporated was used in this evaluation.

3.2.3 Methanol, HPLC grade. This was obtained from Burdick and Jackson for this evaluation.

3.2.4 Water, HPLC grade, Milli-Q filtered water, Millipore Inc.

3.2.5 Zinc sulfate heptahydrate ($ZnSO_4 \bullet 7H_2O$) 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 C_{12}-dien-Zn (II) metal chelate. This was prepared by placing 2.71 grams of 4-dodecyldiethylenetriamine and 2.87 grams of $ZnSO_4 \bullet 7H_2O$ in a liter flask and diluting to volume with water.

3.3 Standard preparation

Prepare butyl ziram stock standards by weighing 10 to 15 mg of butyl ziram. Transfer the butyl ziram to separate 10-mL volumetric flasks, and add chloroform to the mark. Make working range standards of 1.0 to 120 µg/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 x 4.6 mm ECON C8 (3 µm)
Mobile phase:	86% methanol 14% water with 1 mM zinc chelate and 0.13 M ammonium acetate (Ref. 5.3)
Flow rate:	0.5 mL/min
Wavelength:	250 nm
Retention time:	5.1 min
Injection volume:	2.0 µL

3.5.2 Chromatogram (Figure 3.)

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.

3.7 Calculations

3.7.1 Construct a calibration curve (Figure 4.) by plotting detector response versus concentration (µg/mL) of butyl ziram.

3.7.2 Determine the µg/mL of butyl ziram in both sections of each sample and blank from the calibration curve.

3.7.3 Blank correct each sample section by subtracting the µg/mL found in the blank section from the µg/mL found in the corresponding sample section and then add the sample sections together.

3.7.4 Determine the air concentration by using the following formula.

$$\frac{mg}{m^3} = \frac{(\frac{\mu g}{mL})(\text{desorption volume, mL})}{(\text{air volume, L})(\text{desorption effeciency, decimal})}$$

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to butyl 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 *The Condensed Chemical Dictionary 9th ed.*; Hawley, G.G. Ed.; Van Nostrand Reinhold: New York, 1977; p 938.

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; p 5137.

5.3 Karger, B.L.; Wong, W.S.; Viavattene, R.L.; Lepage, J.N.; Davies, G. Journal of Chromatography 1968, 167, 253-272.