Method number:	PV2044
Target Concentration:	5 mg/m^3 OSHA permissible exposure level (PEL).
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 toluene and analyzed by gas chromatography (GC) using a flame photometric detector (FPD).
Recommended air volume and sampling rate:	240 minutes at 1.0 L/min (240 L)
Detection limit of the overall procedure	44 µg/m^3 (based on the recommended air volume and the analytical detection limit):
Status of method:	Partially Validated method. This method has been partially evaluated and is presented for information and trial use only.

July 1990 (final draft)

Duane Lee

Carcinogen and Pesticide Branch
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken because OSHA recently adopted the metribuzin TLV as a PEL. The OVS-2 sampling tube was tested as an effective sampling device for metribuzin. This method follows the procedure developed for some organophosphorus pesticides. (Ref. 5.1)

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_{50} in rats ranges from 1100 to 2300 mg/kg. (Ref. 5.3) An inhalation test in rats at 31 mg/m^3 showed no effects. (Ref. 5.5)

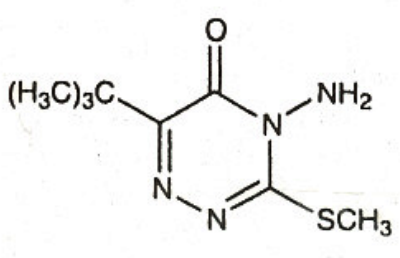
1.1.3 Potential workplace exposure

Metribuzin is used as a selective herbicide. There was no information available on the number of workers exposed to metribuzin.

1.1.4 Physical properties (Ref. 5.2 to 5.5)

CAS number:	21087-64-9
IMIS number:	A175
Molecular weight:	214.3
Molecular formula:	$C_8H_{14}N_4OS$
Melting point:	125-126.5 °C
Solubility:	soluble in methanol, ethanol and glycol ether acetate; soluble in toluene (observed); slightly soluble in water, 1200 ppm
Chemical name:	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-One
Synonyms:	4-amino-6-tert-butyl-3-methylthio-as-triazin-5-one; 4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5-one; Bay 61597; Bay dic 1468; Bayer 94337; Bayer 6159H; Bayer 6443H; Dic 1468; Lexone; Sencor; Sencoral; Sencorer; Sencorex; 1,2,4-triazin-5-one, 4-amino-6-tert-butyl-3-(methylthio)-; 1,2,4-triazin-5(4H)-one, 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-; Zenkor
Description:	white crystalline solid

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 28:1 split ratio, is 0.4 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise. (Figure 1.)

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 two sections of cleaned XAD-2 adsorbent and a 13-mm diameter glass fiber filter. The sampling section and backup section contain 270 and 140 mg respectively. The backup section is retained by two foam plugs and the sampling section is between a 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 it with plastic caps. Wrap each sample end-to-end with an Form OSHA-21 seal.

2.3.5 Record the air volume for each sample, and list any possible interference.

2.3.6 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.

2.3.7 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 23 µL of a 13.326 mg/mL metribuzin standard and allowed to dry overnight in a drawer at ambient temperature. These samples were each desorbed with 2.0 mL of toluene, shaken for 30 min and analyzed as in Section 3. The results are listed in Table 2.4.

able 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
Ex1	306.5	297.1	96.9
Ex2	306.5	294.1	96.0
Ex3	306.5	325.2	106.1
Ex4	306.5	260.7	85.1
Ex5	306.5	308.4	100.6
Ex6	306.5	307.2	100.2

average = 97.5%

2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 23 µL of a 13.326 mg/mL metribuzin standard on the glass fiber filter. These were allowed to dry overnight and then 240 L of humid air (~ 81% relative humidity) were drawn through each tube at 1 L/min. Six of the tubes were each desorbed with 2.0 mL of toluene, shaken for 30 min and then analyzed as in Section 3. The results are listed in Table 2.5. The remaining samples were stored, 6 in a drawer at ambient temperature and 6 in a freezer.

Table 2.5
Retention Efficiency

sample #	µg spiked	µg found	% recovered
R1	306.5	323.5	105.5
R2	306.5	267.3	87.2
R3	306.5	288.9	94.3
R4	306.5	286.3	93.4
R5	306.5	310.1	101.2
R6	306.5	320.2	104.5

average = 97.7%

2.6 Sample storage

After 7 days of storage, 6 tubes, 3 from the ambient storage group and 3 from the freezer storage group, were each desorbed with 2.0 mL of toluene, shaken for 30 min and then analyzed as in Section 3. The remaining tubes were desorbed and analyzed after 9 days of storage. The results are given in Tables 2.6.1 and 2.6.2.

Table 2.6.1
Ambient Storage

sample #	µg spiked	µg found	% recovered
7	306.5	285.5	93.1
7	306.5	302.2	98.6
7	306.5	306.2	99.9
9	306.5	288.3	94.1
9	306.5	337.4	110.1
9	306.5	283.1	92.4

average 7 days = 97.2%
average 9 days = 98.9%

Table 2.6.2
Freezer Storage

sample #	µg spiked	µg found	% recovered
7	306.5	295.6	96.4
7	306.5	320.1	104.4
7	306.5	274.8	89.7
9	306.5	304.1	99.2
9	306.5	334.4	109.1
9	306.5	317.4	103.6

average 7 days = 96.8%
average 9 days = 104.0%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 240 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 metribuzin. 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 A GC equipped with an FPD using a sulfur filter. A Hewlett-Packard (HP) 5890 equipped with an autosampler was used in this evaluation.

3.1.4 A GC column capable of separating metribuzin from any interference. A 30-m × 0.32-mm i.d. (1.0 µm d_f DB-5) capillary column was used in this evaluation.

3.1.5 An electronic integrator or some other suitable means for measuring detector response. The Waters 860 Laboratory Data System was used in this evaluation.

3.1.6 Volumetric flasks and pipettes.

3.1.7 Vials, 2-mL.

3.2 Reagents

3.2.1 Toluene, reagent grade.

3.2.2 Metribuzin, reagent grade. A standard obtained from EPA (EPA #4634, 99.8% purity) was used in this evaluation.

3.3 Standard preparation

Prepare metribuzin stock standards by weighing 10 to 15 mg of metribuzin. Transfer the metribuzin to separate 10-mL volumetric flasks, and add toluene to the mark. Make working range standards of 5.3 to 335 µg/mL by diluting of the stock standards with toluene. Store stock and diluted 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 toluene to each vial and seal with a PTFE-lined cap.

3.4.3 Shake the vials for 30 minutes on a mechanical shaker.

3.4.4 If necessary, transfer the samples to 2-mL vials for use on an HP autosampler.

3.5 Analysis

3.5.1 Instrument conditions

Column: 30-m × 0.32-mm i.d. (1.0 µm d_f DB-5)

Temperatures:

Injector temperature:	250°C
Column temperature:	220°C
Detector temperature:	225°C

Gas flows:

Column (mL/min):	1 hydrogen
FPD make up (mL/min):	42 nitrogen

Injection volume: 2 µL
Split ratio: 28:1
Retention time: 3.06 min

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 GC conditions may generally be varied to circumvent interferences.

3.6.3 Retention time on a single column is not proof of chemical identity. Analysis by an alternate GC column or detector, high performance liquid chromatography (HPLC) 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 metribuzin.

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

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

3.7.4 Determine the air concentration by using the following formula.

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

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to metribuzin.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendation for Further Study

4.1 This method should be fully validated.

4.2 A GC with a nitrogen-phosphorus detector may yield better sensitivity.

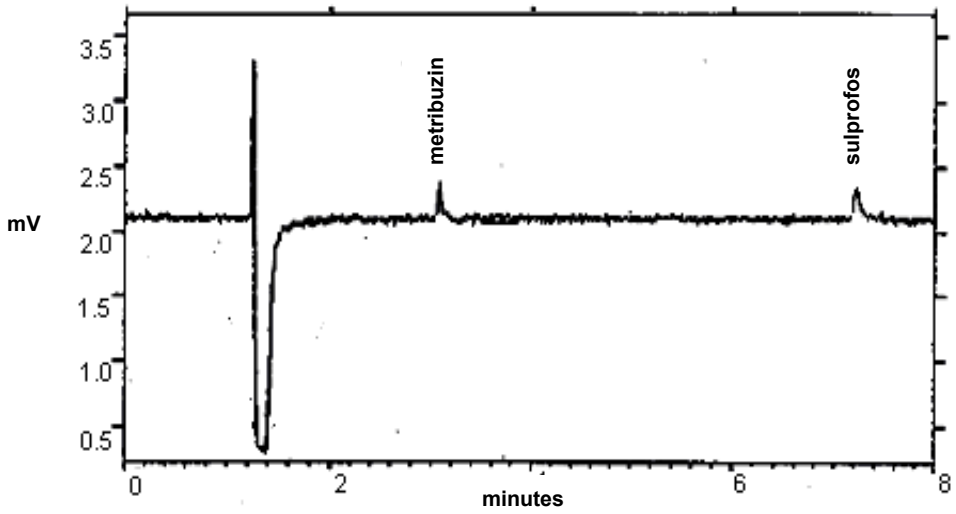


Figure 1.
Detection Limit Chromatogram of Metribuzin and Sulprofos

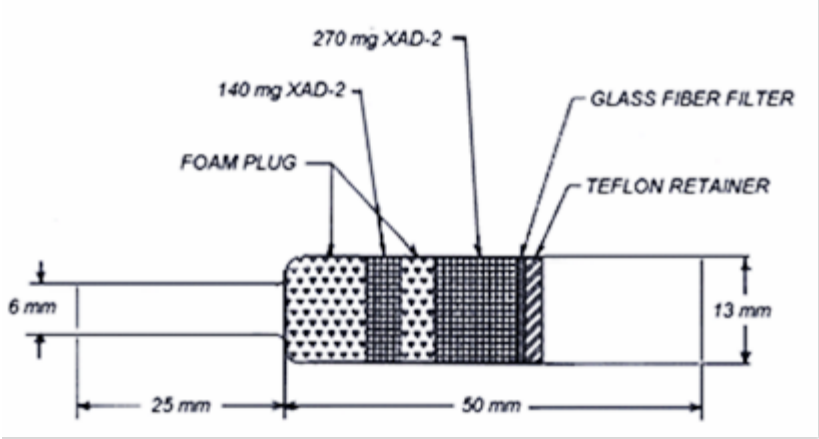


Figure 2.
OVS-2 Sampling Tube

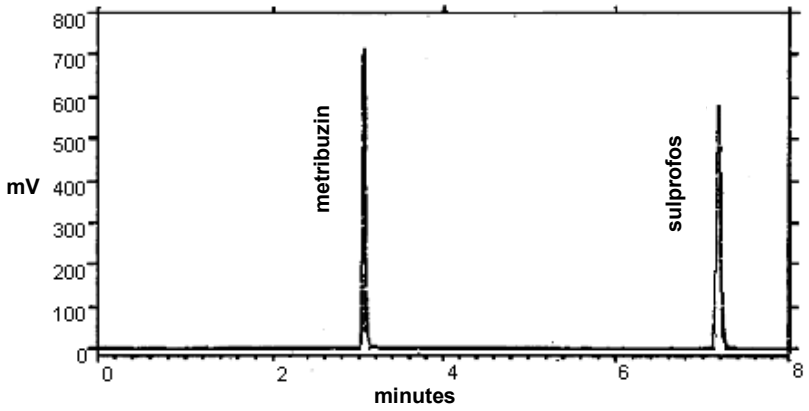


Figure 3.
Chromatogram of Metribuzin and Sulprofos

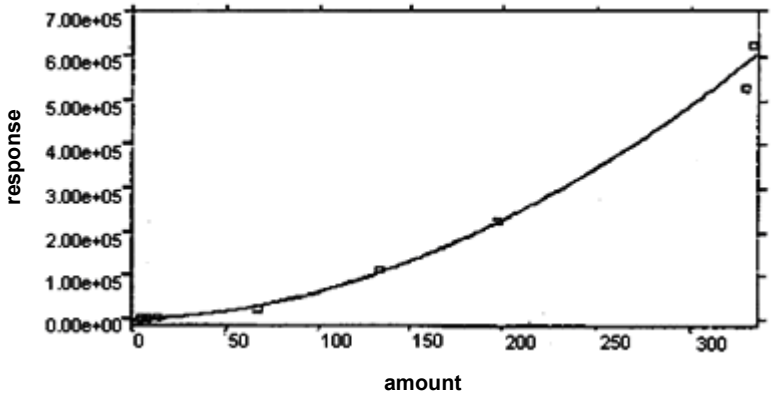


Figure 4.
Calibration Curve

5 References

5.1 Burright, D., Method #62, Chlorpyrifos, DDVP, Diazinon, Malathion, and Parathion, OSHA Analytical Laboratory, unpublished, 1986.

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 4841.

5.3 Farm Chemicals Handbook; Berg, Gordon L. Ed.; Meister: Willoughby, Ohio, 1989; p C195.

5.4 Merck Index, 10th ed.; Windholz, Martha ED.; Merck: Rahway, N.J., 1983; p 881.

5.5 Documentation of Threshold Limit Values and Biological Exposures Indices; American Conference of Governmental Industrial Hygienists Inc., Fifth Edition 1986, p 411.