Crufomate

Method number:	PV2015
Target Concentration: OSHA PEL	5 mg/m^3
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:	60 minutes at 1.0 L/min (60 L)
Detection limit of the overall procedure	57 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.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken because OSHA recently adopted the TLV's as PEL's. The OVS-2 sampling tube was tested as an effective sampling device for crufomate. This method follows the procedures developed for other 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.)

Crufomate is used as an insecticide for cattle grubs, horn flies, and lice. The oral LD_{50} in rats ranges from 460 to 770 mg/kg. (Ref. 5.2 and 5.3)

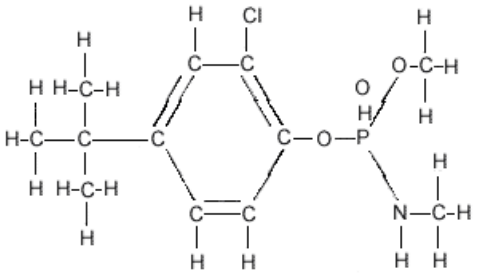
1.1.3 Potential workplace exposure

There was no information available on the number of workers exposed to crufomate. There was an estimated 2×10^8 grams produced in the U.S. in 1972. (Ref. 5.6)

1.1.4 Physical properties (Ref. 5.2 to 5.5)

CAS number:	299-86-5
IMIS number:	0776
Molecular weight:	291.71
Molecular formula:	$C_{12}H_{19}ClNO_3P$
melting point:	60-60.5 °C
Solubility:	soluble in benzene, acetone, carbon tetrachloride; practically insoluble in water, light petroleum
Chemical name:	4-tert-butyl-2-chlorophenyl n-methyl o-methylphosphoramidate
Synonyms:	Dowco 132; Montrel; Ruelene; crufomat; phosphoramidic acid, 4-tert-butyl-2-chlorophenyl-phosphoramidate; Rulene 25E
Description:	white crystals

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 28:1 split ratio, is 0.061 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, with the large end facing down, 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.

2.3.5 Wrap each sample end-to-end with a Form OSHA-21 seal.

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

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 21 µL of a 14.339 mg/mL crufomate standard and allowed to dry overnight in a drawer at ambient temperature. These samples were then desorbed with 2.0 mL of toluene containing triphenyl phosphate (TPP) as the internal standard, shaken for 30 min, and analyzed as in Section 3. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
1	301.12	266.23	88.4
2	301.12	283.23	94.1
3	301.12	264.41	87.8
4	301.12	284.98	94.6
5	301.12	281.82	93.6
6	301.12	277.54	92.2

average = 91.8%

2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 21 µL of a 14.339 mg/mL crufomate standard on the glass fiber filter. These were allowed to dry overnight and then 480 L of humid air (~77% relative humidity) were drawn through each tube at 1 L/min. Six of the tubes were then desorbed immediately with 2.0 mL of toluene containing TPP, 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
1	301.12	262.68	87.2
2	301.12	275.75	91.6
3	301.12	265.09	88.0
4	301.12	266.73	88.6
5	301.12	263.01	87.3
6	301.12	279.17	92.7

average = 89.2%

2.6 Sample storage

After 3 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 containing TPP, shaken for 30 min and then analyzed as in Section 3. The remaining tubes were desorbed and analyzed after 10 days of storage. The results are given in Tables 2.6.1 and 2.6.2.

Table 2.6.1
Ambient Storage

days stored	µg spiked	µg found	% recovered
3	301.12	270.67	89.9
3	301.12	271.11	90.0
3	301.12	263.66	87.6
10	301.12	250.69	83.3
10	301.12	278.80	92.6
10	301.12	264.13	87.7

average of ~3 days = 89.2%
average of ~10 days = 87.9%

Table 2.6.2
Freezer Storage

days stored	µg spiked	µg found	% recovered
3	301.12	262.01	87.0
3	301.12	279.06	92.7
3	301.12	281.03	93.3
10	301.12	262.02	87.0
10	301.12	185.56	61.6
10	301.12	274.46	91.1

average of ~3 days = 91.0%
average of ~9 days = 79.9%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 60 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 crufomate. 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.

3.1.2 A mechanical shaker.

3.1.3 A GC equipped with an FPD. A Hewlett-Packard (HP) 5890 equipped with an FPD and an autosampler.

3.1.4 A GC column capable of separating crufomate from any interference. A 30-m × 0.32-mm i.d. (1.0 µm d_f DB-5) capillary column.

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

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 Crufomate, reagent grade. A standard was obtained from EPA (EPA # 6020, 98.89% purity).

3.2.3 Triphenyl phosphate, reagent grade. A 40 µg/mL solution of TPP in toluene was used as an internal standard.

3.3 Standard preparation

Prepare crufomate stock standards by weighing 10 to 15 mg of crufomate. Transfer the crufomate to separate 10-mL volumetric flasks, and add toluene to the mark. Make working range standards of 1.7 to 300 µg/mL by pipette dilutions of the stock standards with toluene containing TPP. 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 containing TPP 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 Transfer, if necessary, the samples to 2-mL vials for use on an HP autosampler.

3.5 Analysis

3.5.1 Instrument conditions

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

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

Gas flows:
Column: 1 mL/min hydrogen
FPD make up: 42 mL/min nitrogen

Injection volume: 1 µL

Split ratio: 28:1

Retention time: 6.3 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, 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 crufomate.

3.7.2 Determine the µg/mL of crufomate 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 crufomate.

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.

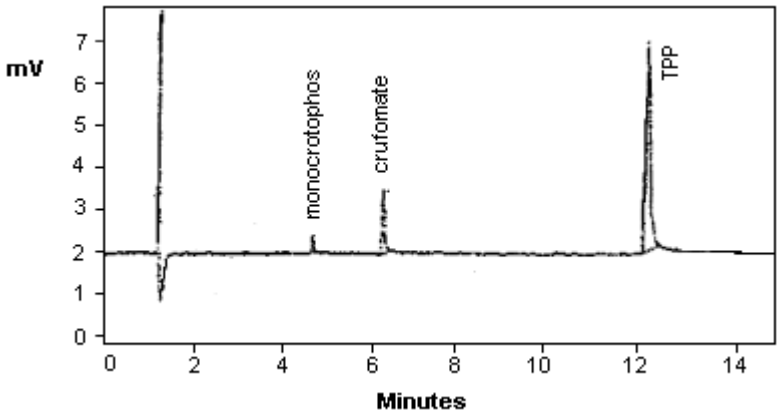


Figure 1.
Detection Limit Chromatogram of Crufomate with Monocrotophos and TPP

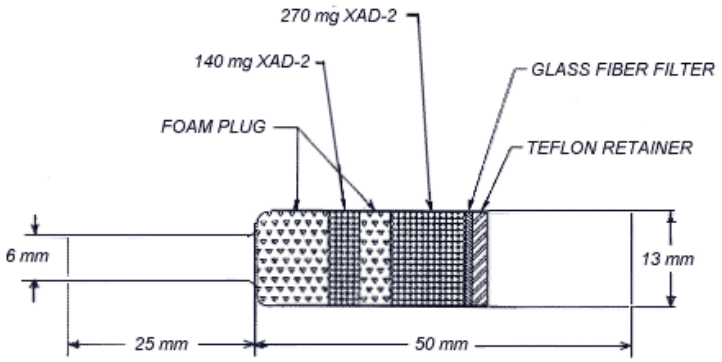


Figure 2.
OVS-2 Sampling Tube

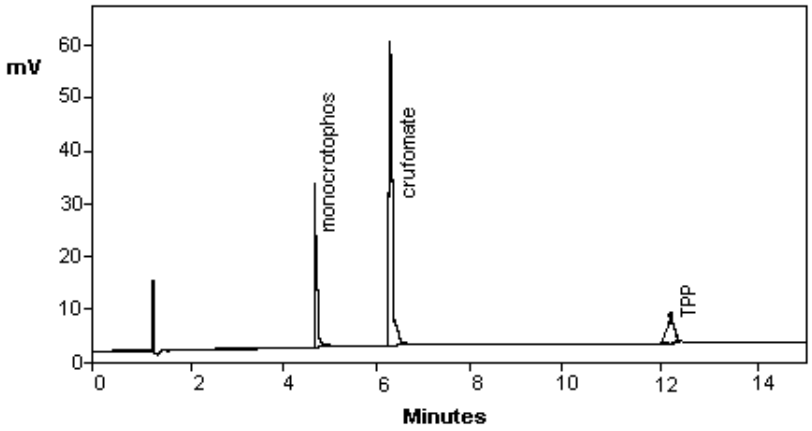


Figure 3.
Chromatogram of Crufomate with Monocrotophos and TPP

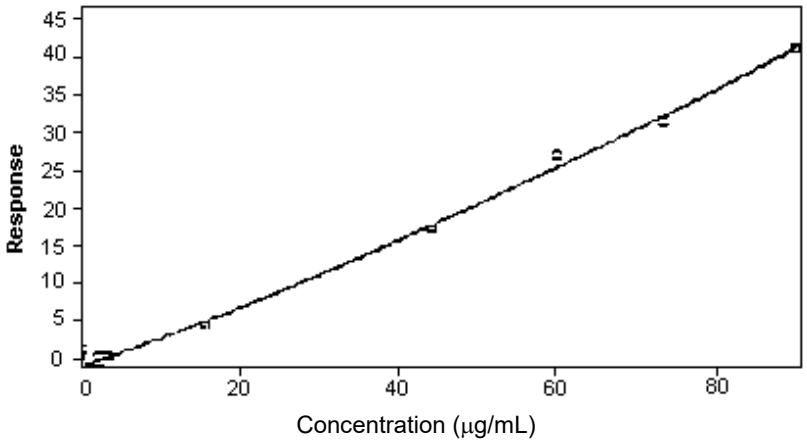


Figure 4.
Calibration Curve

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; pp. 3375-6.

5.3 Farm Chemicals Handbook; Berg, Gordon L. Ed.; Meister: Willoughby, Ohio, 1985; p C206.

5.4 Merck Index, 10th ed.; Windholz, Martha ED.; Merck: Rahway, N.J., 1983; p 373.

5.5 Documentation of Threshold Limit Values and Biological Exposures Indices; American Conference of Governmental Industrial Hygienists Inc., Fifth Edition 1986, p 150.

5.6 HSDB (Hazardous Substance Data Base)