Method number:	PV2097
Target concentration:	10 mg/m^3 (ACGIH TLV-TWA)
Procedure:	Samples are collected by drawing a known volume of air through an OSHA versatile sampler (OVS-2) tube, containing a glass fiber filter and two sections of XAD-2 absorbent. Samples are desorbed with acetonitrile and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.
Recommended air volume and sampling rate studied:	60 minutes at 1.0 L/min (60 L)
Detection limit of the overall procedure	0.03 mg/m^3 (based on the recommended air volume)
Special Requirements:	Protect samples from light until analyzed.
Status of method:	Partially validated method. This method has been only 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 to determine the effectiveness of the OVS-2 tube for sampling diuron and for analyzing samples. It follows the method developed for carbaryl. (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).

Herbicides are weed killers with either general or selective applications in agriculture. Herbicides interfere with plant chemistry and physiology. They may inhibit plant respiration and photosynthesis, as well as plant physiology by mimicking growth regulators or interfering with their synthesis or action. Diuron is an herbicide whose chemical class is phenyl urea. It has been shown to inhibit plant photosynthesis by blocking light reaction II. Hence, light is required to elicit its phototoxic effects. This herbicide demonstrates low acute toxicity toward mammals. (Ref. 5.2) The following paragraph describing the toxicity is excerpted from the book Documentation of the Threshold Limit Values and Biological Exposure Indices (Ref. 5.3)

Hodge and co-workers have reported a low order of acute and chronic toxicity for diuron. The oral LD_{50} for male rats was given at 3400 mg/kg. No-effect dietary concentration levels in two-year feeding studies are considered to be 250 ppm for rats and 125 ppm for dogs. A dietary concentration of 125 ppm did not adversely affect reproduction in a three-generation rat study. There was no evidence of carcinogenicity in these chronic studies or in an 18-month study on mice at approximately 1400 ppm.

The following paragraph describing the harm and symptoms of diuron was taken from the Handbook of Toxic and Hazardous Chemicals and Carcinogens. (Ref. 5.4)

The concentrated material may cause irritation to the eyes and mucous membranes, but a 50% water paste was not irritating to the intact skin of guinea pigs. Due to these factors, diuron has been given a TLV-TWA of 10 mg/m^3 by the ACGIH. (Ref. 5.3) OSHA adopted this same value as its PEL in March 1989. Editorial Note: These March 1989 PELs were vacated on July 7, 1992 and ceased to be enforceable on March 23, 1993 (FR 58:35338-35351, 6/30/1993).

1.1.3 Potential workplace exposure

No estimate of worker exposure to diuron could be found. Potential exposure involves those individuals in manufacturing, formulation, and application of the herbicide. (Ref. 5.4)

1.1.4 Physical Properties (Ref. 5.2 - 5.7)

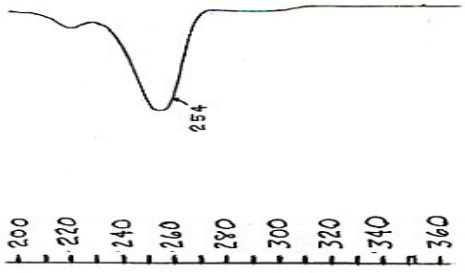
CAS #:	330-54-1
IMIS #	2684
Molecular weight:	233.10
Molecular Formula:	$C_9H_{10}Cl_2N_2O$
Melting point:	158 to 159 °C
Vapor Pressure:	0.0041 Pa (0.000031 mmHg) at 30 °C
Appearance:	white crystalline solid

Solubility: 42 ppm in water at 25 °C, 5.3% at 27 °C, very low solubility in hydrocarbon solvents

Synonyms: Cekiuron, Crisuron, Dailon, Diater, Di-on, Direx 4L, Diurex, Diurol, Dynex, Karmex, Rout, Unidron, Urox D, Vonduron, dichlorfenidim (USSR)

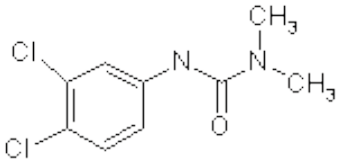
Chemical names: 3-(3,4-Dichlorophenyl)-1,1-dimethylurea; N'-(3,4-dichlorophenyl)-N,N-dimethylurea

UV spectrum:



Stability: Sunlight (ultraviolet irradiation) degrades diuron. Decomposes on heating (180-190 °C) yielding dimethylamine and 3,4-dichlorophenylisocyanate.

Structural Formula:



1.2 Limiting defining parameters

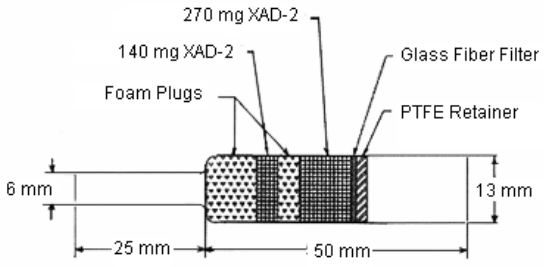
The detection limit of the analytical procedure is 1.81 ng per injection. This is the amount of amount of analyte which will give a peak whose height is approximately five times the baseline noise.

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



2.2 Reagents

No sampling reagents are required.

2.3 Sampling Technique

2.3.1 Attach the small end of the OVS-2 sampling tube to the sampling pump with flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler.

2.3.2 Attach the sampler vertically (large end down) in the worker's breathing zone in such a manner that it does not impede work performance.

2.3.3 After sampling for the appropriate time, remove the sampling device and seal the tube with plastic end caps.

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

2.3.5 Submit at least one blank with each set of samples. Handle the blank the same as the other samples but do not draw air through it.

2.3.6 Submit any bulk samples in a separate container. Do not ship bulks with the air samples.

2.4 Extraction efficiency

Three OVS-2 tubes were each liquid spiked with 31 µL (1/20 PEL) of a 0.9627 mg/mL solution of diuron in acetonitrile. Three additional OVS-2 tubes were each liquid spiked with 62 µL (1/10 PEL) of the above diuron standard. These tubes were allowed to sit overnight on a desk at ambient temperature, then extracted with 5.0 mL of acetonitrile, and analyzed as in Sections 3.4 and 3.5.

Table 2.4
OVS-2 Extraction Study

tube #	1/20 PEL %	1/10 PEL %
1	96.6	86.6
2	88.1	96.3
3	91.7	95.0
average	92.1%	92.6%

2.5 Retention efficiency

Four OVS-2 tubes were each liquid spiked with 62 µL of a 0.9627 mg/mL solution of diuron by spiking the glass fiber filter. Sixty liters of humid air (approximately 70% relative humidity) were drawn through each tube. Three of these tubes were then desorbed and analyzed as in Sections 3.4 and 3.5. No diuron was recovered from the backup section of these tubes. The fourth tube had 120 liters of humid air drawn through it and had a recovery of 91.9%.

Table 2.5
Retention Efficiency Study

tube #	recovery %
1	95.6
2	91.0
3	95.5
average	94.0%

2.6 Sample storage

Eighteen OVS-2 tubes were each liquid spiked with 62 µL of a 0.9627 mg/mL solution of diuron by placing it on the glass fiber filter. Sixty liters of humid air (approximately 70% relative humidity) were drawn through each tube. Half of the tubes were stored in a drawer at ambient temperature, and the other half were stored in a refrigerator (2 °C). They were stored according to Table 2.6 and extracted and analyzed as in Section 3.4 and 3.5. No diuron was recovered from the backup section of these tubes.

Table 2.6
Storage Study

day	ambient	average	refrigerated	average
0	95.7		96.2	
0	97.1		96.7	
0	95.9	96.2%	96.1	96.3%
7	94.2		95.3	
7	93.3		95.0	
7	95.6	94.4%	94.8	95.0%
14	94.1		96.2	
14	91.6		95.8	
14	91.7	92.5%	95.0	95.7%

Average recovery (ambient) 94.4%
Average recover (refrigerator) 96.0%

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 diuron. Suspected interferences should be reported to the laboratory with submitted samples.

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 An HPLC equipped with a UV detector and a manual or automatic injector. A Waters 6000 pump, Waters 712 autosampler, and Waters 490E UV detector were used in this evaluation.

3.1.2 An HPLC column capable of separating diuron from any interference. A (8-cm x 6.2-mm i.d.) Golden Series 3-µm Zorbax ODS column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 3357 Data System was used in this evaluation.

3.1.4 Vials, 4-mL and 20-mL glass with capped PTFE-lined septa.

3.1.5 Volumetric flasks, pipettes, and syringes.

3.2 Reagents

3.2.1 Acetonitrile, HPLC grade.

3.2.2 Water, HPLC grade. A Millipore Milli-Q system was used to prepare the water in this evaluation.

3.2.3 Diuron. A 99.25% pure standard from EPA was used in this evaluation.

3.3 Standard preparation

Prepare stock standard solutions by adding acetonitrile to pre-weighed amounts of diuron. Prepare working range standards by diluting stock solutions with acetonitrile. 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 OVS-2 tube to a 20-mL vial. Place the first foam plug and the 140-mg backup section in a separate 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 5.0 mL of acetonitrile to each vial.

3.4.3 Seal the vials and shake them for half an hour on a mechanical shaker.

3.4.4 Transfer an aliquot of sample to the 4-mL vial and seal with capped PTFE-lined septa.

3.5 Analysis

3.5.1 Liquid chromatographic conditions

Column:	8-cm x 6.2-mm i.d. stainless steel Golden Series column packed with 3- µm Zorbax ODS
Mobile Phase:	55% acetonitrile / 45% water
Flow Rate:	1 mL/min
UV detector:	254 nm
Retention time:	5.44 min
Injection volume:	15 µL

3.5.2 Chromatogram

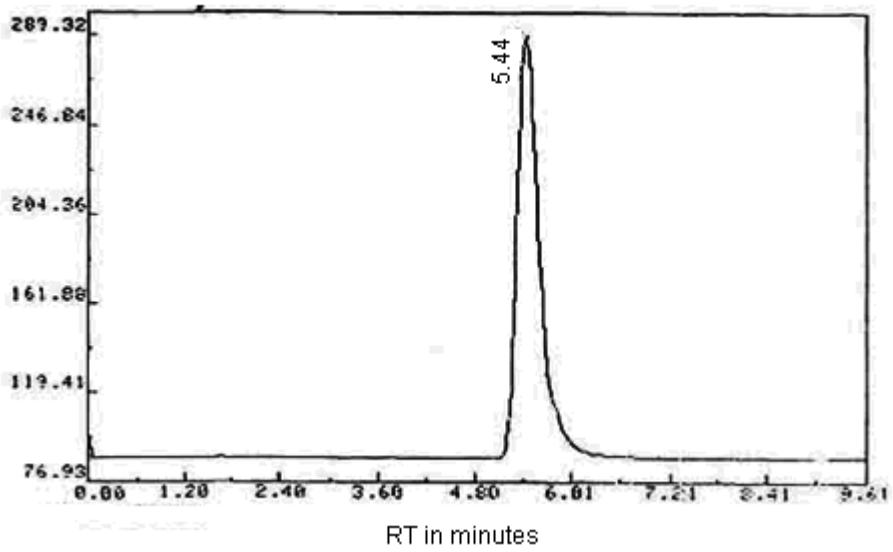


Figure 3. Chromatogram of Diuron

3.6 Interferences (analytical)

3.6.1 Any compound having a retention time similar to that of the analyte is a potential interference. Generally, chromatographic conditions can be altered to separate interferences from the analyte.

3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate HPLC column, detection at another wavelength (for comparison of absorbance response ratios) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus standard concentration.

3.7.2 Determine the concentration of diuron in each sample from the calibration curve. If diuron is found on the backup section, make blank corrections for each section separately before adding the results together.

3.7.3 Determine the air concentration by 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 exposure to all standards.

3.8.2 Avoid exposure to all solvents.

3.8.3 Wear safety glasses, gloves, and lab coat at all times in laboratory areas.

4 Recommendations for Further Study

4.1 A better desorption solvent than acetonitrile might be found.

4.2 This method should be fully validated.

4.3 This method has been partially evaluated at 60 liters or air at 1 liter per minute; however, since the PEL of diuron is high and its solubility is low, it might be better to lower the sampling rate to 0.2 L/min to prevent the sampling tube from becoming clogged with diuron.

5 References

5.1 Burright, D.; Method #63, "Carbaryl"; OSHA Analytical Laboratory unpublished, 1987.

5.2 Cawse, J.N.; "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed.; John Wiley and Sons: New York, NY., 1980; Vol. 12, pp 297-322.

5.3 Documentation of the Threshold Limit Values and Biological Exposure Indices," 5th ed.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1986; p 228.

5.4 Sittig, M.; "Handbook of Toxic and Hazardous Chemical and Carcinogens," 2nd ed.; Noyes Publication: Park Ridge, N.J., 1985; p 394.

5.5 "Farm Chemicals Handbook"; Meister Publishing Co.: Willoughby, OH, 1986; p C88.

5.6 "Merck Index," 10th ed.; Windholz, M., Ed.; Merck and Co.: Rahway, NJ, 1983; p 494.

5.7 Cawse, J.N.; "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed.; John Wiley and Sons: New York, NY., 1980; vol. 21 pp 273-276.