

Determination of Chloropicrin Desorbed from XAD-4 Resin Tubes

1. Scope:

This method describes the desorption and determination of chloropicrin from XAD-4 air sample tubes.

2. Principle:

Chloropicrin in the air that has been adsorbed onto XAD-4 resin is desorbed from the resin with hexane. Subsequently, chloropicrin is quantified using a gas chromatograph with an Electron Capture Detector (ECD).

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Hexane is a flammable and toxic solvent; it should be handled with care in a ventilated area.

4. Interferences:

There were no interferences at the time of validation for the background provided.

5. Apparatus and Equipment:

5.1 Test tubes, 50 mL, 25 mL with Teflon-liner caps

5.2 Pasture pipettes and micro-syringes

5.3 Volumetric flasks, various sizes

5.4 Thermolyne Vortex Maxi Mixer II

5.5 Volumetric pipettes, various sizes

5.6 Funnel, short stem and large exit diameter fits into the extraction test tube

5.7 Files or Dremel (an electric rotary flex shaft tool) with $\frac{3}{4}$ " diamond saw

5.8 Autosampler vial, 2 mL

6. Reagents and Supplies:

6.1 Hexane, pesticide residue grade

6.2 Chloropicrin, CAS# 76-06-2

6.3 XAD-4 resin, obtained from Rohm and Hass, packed in Lo-Vol tubes

6.4 Sorbent tubes XAD-4, SKC Inc. # 226-175

7. Standards Preparation:

- 7.1 A 1.0 mg/mL chloropicrin standard was obtained from the CDFA/CAC Standard Repository. Working standards were prepared to cover the linear range of 0.005 µg/mL to 1.0 µg/mL
- 7.2 Keep all standards in the designated refrigerator for storage.
- 7.3 The expiration date of each standard is six months from the preparation date.

8. Sample Preservation and Storage:

Store all samples waiting for extraction in a designated freezer. Extracts shall be stores in a designated refrigerator (4 ± 3 °C).

9. Test Sample Preparation for :

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the resin and SKC tubes used in method validation and QC. The resin was washed following SOP # EMON-SM-05-002 with acetone and hexane as the wash solvents. Lo-Vols were packed according to DPR's SOP FSA1001.00 .

9.2 Preparation of blank and spikes:

Matrix blank lo-vols: no special requirements

Matrix spike lo-vols: Spike a known amount of chloropicrin using a micro-syringe. Place the mirco-syringe needle about 0.5 cm below the glass wool layer and spike. Allow the spike to set for 4-6 minutes before following the test sample extraction procedure for lo-vol tubes.

Matrix blank SKC: Score the tube with a file or Dremel just above the glass wool plug
Snap the tube. Score the tube at the tip end and snap to remove tip. Follow the test sample extraction procedure.

Matrix spike SKC: Score the tube with a file or Dremel just above the glass wool plug. Snap the tube. Score the tube at the tip and snap to remove tip. Spike a known amount of chloropicrin using a micro-

syringe. Place the micro-syringe needle about 0.5 cm below the glass wool plug and spike. Allow the tube to set for 4-6 minutes before following the test sample extraction procedures for SKC tubes.

9.3 Test Sample Extraction of Lo-Vol

- 9.3.1 Remove samples from freezer. Allow samples to come to room temperature for 20-30 minutes before extraction.
- 9.3.2 Place a funnel in the sample extraction tube, Remove the top glass wool from the XAD-4 sampling tube using a forceps. Push the glass wool down into the extraction tube. Pour the resin into the extraction tube via a funnel. Tap the side of sampling tube to allow adhered resin beads to drop into the extraction tube. Using the pipette, push the bottom glass wool and metal screen into the extraction tube.
- 9.3.3 Pipette a known volume of hexane and wash the inside wall of the sampling tube into the extraction tube. A volume of 10 mL hexane for tube containing 10 mL XAD-4 resin is suggested.
- 9.3.4 Extract chloropicrin from XAD-4 by mixing for 60 seconds on a vortex mixer.
- 9.3.5 Allow the mixture at room temperature for 1-2 minutes. Transfer about 1 mL extract from the bottom of the tube into an autosampler vial and cap it tightly. Store extract in a second autosampler vial is recommended.
- 9.3.6 Determine chloropicrin using a gas chromatograph with electron capture detector.

9.4 Test Sample Extraction of Sorbent tubes

- 9.4.1 Remove samples from freezer. Allow samples to come to room temperature for 20-30 minutes before extraction.
- 9.4.2 Fold a sheet of paper into quarters, reopen and place under the tube to catch any resin spills.
- 9.4.3 Pipet 10 mL of hexane into a labeled extraction test tube.

- 9.4.4 Remove caps from sorbent tubes and score the tube with a file or Dremel just above the glass wool plug. Snap the sorbent tube: remove the glass wool plug with forceps. Transfer the glass wool plug to the tube containing the hexane.
- 9.4.5 Place the large open end of the sorbent tube into the mouth of the test tube and tap the sorbent tube to remove the resin.
- 9.4.6 Score and snap the sorbent tube again to get the second glass wool plug. Remove wool plug and add rest of resin to the same test tube.
- 9.4.7 Vortex the sample for 60 seconds and then allow it to sit for 4-5 minutes.
- 9.4.8 Transfer the extract into an autosampler vial for GC analysis.

10. Instrument Calibration:

The calibration standard curve consists of a minimum of three levels. The recommended concentrations levels of standards are 0.005, 0.02, 0.1, 0.05 and 1.0 ug/mL. Calibration is obtained using a quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

11. Analysis:

11.1 Injection Scheme

The instrument may need to be conditioned with a standard a couple of times before running the following sequence of Standard Curve, Hexane, Matrix Blank, Matrix Spike, Test Samples (maximum of 10-12) and Standard Curve.

11.2 GC-ECD

11.2.1 Gas Chromatograph: Agilent micro ECD
Column: DB-5ms (5% phenyl-methyl polysiloxane)30 m x 0.25 mm x 1.0um

Temperature Program: initial column temperature 40°C, hold for 5 min., ramp at 10°C/min. to 140°C hold for 0 min., ramp at 30°C/min. to 210°C hold for 1 min..

Injector Temperature: 200°C

Injection volume: 2 uL

Carrier Gas: Helium

Column Head Pressure: 10.5 psi, Flow rate: 0.63mL/min.

Detector Temperature: 350°C

Retention time: 12.8 ± 0.1 minute

12. Quality Control:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 sample tubes are spiked individually with 0.2 µg of chloropicrin. These spiked samples along with a blank are analyzed using the described method. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL using the following equation:

$$\text{MDL} = tS$$

Where t is the Student t value for the 99% confidence level with n - 1 degrees of freedom and S denotes the standard deviation obtained from n replicates analyses. For the n=7 replicates used to determine the MDL, t=3.143. The results for the standard deviations and MDL shown below:

<u>Spike</u>	<u>µg Spiked</u>	<u>µg Recovered</u>
1	0.2	0.156
2	0.2	0.161
3	0.2	0.159
4	0.2	0.166
5	0.2	0.164
6	0.2	0.167
7	0.2	0.172

Average µg Recovered = 0.164

Standard Deviation = 0.005

The calculated MDL for chloropicrin is 0.016 µg.

The MDL was established on Lo-Vol tube

12.2 Reporting Limit (RL)

Reporting Limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The reporting limit for chloropicrin is 0.2 ug per sample tube.

12.3 Method Validation

Method Validation was done on two different types of tubes, lo-vols and sorbent tubes. The method validation consisted of five sample sets for lo-vol tubes and 3 sets for sorbent tubes. Each set included three levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for chloropicrin are tabulated in Appendix 1.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each type of tube. The upper and lower control limits are set at ± 3 standard deviations of the % recovery, shown in Appendix 2

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time should be within ± 2 percent of that of the standards.

12.5.3 The recoveries of the matrix spikes shall be within the control limits.

12.5.4 The sample shall be diluted if results exceed the calibration curve.

13.0 Calculations:

Results are generally calculated by Hewlett Packard ChemStation software using its quadratic curve fit option with all levels weighted equally. Alternatively, results are calculated manually using the formula below:

$$\mu\text{g Chloropicrin} = \frac{(\text{peak ht sample}) (\text{ng std injected}) (\text{sample final volume, mL})}{(\text{peak ht standard}) (\mu\text{L injected})}$$

14.0 Reporting Procedure:

Sample results are reported in accordance with the client's analytical laboratory specification sheets.

15.0 Discussion:

15.1. Injector port temperature should be set at 200°C. It was noticed that when injector temperature was set at 240°C, chloropicrin converts to the dimer (hexachloroethane) completely.

- 15.2 For a better sensitivity, one should use EC detector. However, MSD SIM mode is a good tool for confirmation. Confirmation to the level 0.5 µg chloropicrin per sample has been achieved.
- 15.3 The use of SKC tubes was added to this method at the revised date. The MDL and RL were established from the original data generated from the Lo-Vol tubes.

16.0 References:

- 16.1 *NIOSH Manual of Analytical Methods, Second Edition Method S212, S104, 260.* Available from Superintendent of Documents, US. Government Printing Office, Washington, DC, 20402
- 16.2 Guide to Chemicals used in Crop Production, Information Canada, P. 118, 1973
- 16.3. Scott Fredrickson, CDFA, *The analysis of air samples for chloropicrin*, Center for Analytical Chemistry, Worker and Health Safety, February 2, 1982.
- 16.4. James Seiber, Final Report to the Air Resources Board Pilot Analysis of Chloropicrin in Air, Contract #A5-169-43. Dated October 28, 1987.
- 16.5. J&W Scientific Catalog and Reference Guide 1994-95, P.159.

Appendix 1

Method validation for Lo-Vol tubes

Analyte	spike ug/sample	Recovery set 1	Recovery set 2	Recovery set 3	Recovery set 4	Recovery set 5	Control Limits
chloropicrin	1	75.7	82	83	89.3	86.4	UCL: 100
	10	87.4	78	75.6	86.2	83.9	LCL:65.8
	100	88.9	77	74	91.2	88.7	Mean:83.2

Method Validation for SKC 226 -175-tubes

Analyte	spike ug/sample	Recovery set 1	Recovery set 2	Recovery set 3	Control Limits
chloropicrin	1	93.5	95.2	96.5	UCL:102
	12.9	89.9	85.3	93.8	LCL:82
	109	89.7	92.4	93.6	Mean:92.2

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