



Chloropicrin

Method no.: PV2103

Target concentration: 0.1 ppm (0.7 mg/m³) OSHA TWA PEL

Procedure: Samples are collected by drawing a known volume of air through two XAD-4 tubes in series. Samples are desorbed with ethyl acetate and analyzed by gas chromatography with electron capture detector (GC-ECD).

Air volume and sampling rate studied: 25 minutes at 0.2 liters per minute, (5 L)

Special Requirements: Chloropicrin is light sensitive. Samples should be protected from light after sampling by covering them with opaque tape, such as masking tape, and then the Form OSHA-21 seal. Analytical standards and desorbed samples should be protected from light by placing in brown bottles and vials. Bulk samples should be protected from light by placing in brown bottles, or wrapping the bottle with an opaque tape.

Status of method: Partially validated method - This method has been only partially evaluated and is presented for information and trial use.

November, 1991

Mary E. Eide

Organic Service Branch I
OSHA Salt Lake Technical Center
Salt Lake City UT-84115

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Technical Center has received many requests for a sampling and analytical procedure for chloropicrin. Desorption studies using charcoal tubes, and Anasorb 747 showed 2.1% and 25.9% recoveries respectively. The following tubes showed good desorption efficiencies using 1 mL ethyl acetate: XAD-4 (99.6%), XAD-7 (95.9%), Carbosieve S-III (103%), Porapak S (96.9%), and Porapak R (98.3%). Many of these tubes showed breakthrough or poor retention. The XAD-4 tube had good retention and was chosen for this study. Two XAD-4 tubes in series had no chloropicrin on the backup portion of the second tube when 5 liters of 90% RH air was drawn through them. The 14-day storage study showed good recoveries for the samples stored under ambient, dark conditions, but showed an 8.4% loss when stored under room lights. Chloropicrin is light sensitive, and the samples should be protected from light after collection as illustrated by the storage at ambient conditions in room light.

1.1.2 Potential workplace exposure (Ref. 5.1)

Chloropicrin is used as a larvacide, disinfecting cereals and grains, fumigant, soil insecticide, grass, and weed seed killer, as a war gas, and in synthesis. The US production for 1982 was 2.91×10^9 grams.

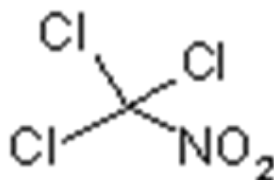
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.2)

Chloropicrin is a skin and eye irritant and lachrymator causing irritation at concentrations as low as 0.3 ppm in humans, depending on individual susceptibility. A concentration of 15 ppm could not be tolerated by any of the test subjects. Chloropicrin causes irritation of upper respiratory passages followed by edema and pneumonia. Gastrointestinal effects are nausea, vomiting, colic, and diarrhea. Lethal rat doses were 340 ppm for 1 minute, or 110 ppm for 20 minutes. Reported human oral lethal dose ranges from 5 to 50 mg/kg.

1.1.4 Physical properties (Ref. 5.1):

CAS: 76-06-2
IMIS: 0675
RTECS: 48193 (PB6300000)

Chemical Structure:



Synonyms: trichloronitromethane; acquinite; nitrochloroform; Larvacide 100; Picfume; chlor-o-pic; dojyopicrin; dolochlor; microlysin; pic-chlor; picride
Molecular weight: 164.39
Density: 1.6558
Freezing point: -64 °C

Boiling point:	112 °C
Odor:	pungent (threshold is 1.1 ppm)
Color:	white to pale yellow oily liquid
Molecular formula:	CCl_3NO_2
DOT:	UN1580: NA1583

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 0.01 ng, with a 1- μL injection volume. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.298 ppb based on a 5-liter air volume. (All ppm amounts in this study are based on a 5-L air volume.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

Samples and analytical standards must be protected from the light.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow.

2.1.2 Sampling tubes containing XAD-4 resin. A sampling tube consists of two sections of XAD-4 resin separated by a glass wool plug or polyurethane plug. The front section contains 80 mg and the backup section 40 mg. The sections are held in place with glass wool plugs in a glass tube 7-cm x 4-mm i.d. length, SKC, or equivalent.

2.2 Sampling technique

2.2.1 Open the ends of the XAD-4 tubes immediately before sampling.

2.2.2 Connect two tubes together and connect them to the sampling pump with flexible tubing.

2.2.3 Place the tubes in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the XAD-4 tubes.

2.2.5 Separate the XAD-4 tubes and seal with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal. Protect samples from light.

- 2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it. Protect sample from light
- 2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.
- 2.2.8 Bults submitted for analysis must be shipped in a separate container from other samples. Protect sample from light.

2.3 Desorption efficiency

Six tubes each were liquid spiked at loadings of 0.338 µg (0.0101 ppm), 1.69 µg (0.0503 ppm), 3.48 µg (0.104 ppm), and 6.95 µg (0.207 ppm) chloropicrin. They were allowed to equilibrate overnight at room temperature. They were opened, each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-ECD. The overall average was 99.8 %.(Table 2.3)

Table 2.3
% Desorption Efficiency

tube #	0.338 µg	1.69 µg	3.48 µg	6.95 µg
1	101	100	99.7	98.9
2	96.4	103	99.9	98.7
3	102	100	100	99.2
4	101	97.9	99.6	98.8
5	99.2	99.3	99.6	98.9
6	101	102	98.6	99.0
average	100	100	99.6	99.0

overall average = 99.8%
standard deviation = ±1.42

2.4 Retention efficiency

2.4.1 Six tubes were liquid spiked with 6.95 µg (0.207 ppm) chloropicrin and allowed to equilibrate overnight. The next day a second XAD-4 tube was attached, and 5 liters humid air (90% RH) was pulled through them at 0.1 L/min. The tubes were opened, desorbed with ethyl acetate, and analyzed by GC-ECD. The retention efficiency averaged 98.9%. There was no chloropicrin found on the backup portions of the second tubes. (Table 2.4.1)

Table 2.4.1
Retention Study With 5 L

tube #	% recovery				total
	front tube		back tube		
	'A'	'B'	'A'	'B'	
1	76.5	16.3	7.1	0.0	99.9
2	89.7	8.9	2.4	0.0	101
3	74.6	15.8	7.6	0.0	98.0
4	90.7	5.5	1.8	0.0	98.0
5	77.1	14.8	6.2	0.0	98.1
6	83.9	10.4	4.0	0.0	98.3

overall average = 98.9%

2.4.2 Four tubes were liquid spiked with 5.96 µg (0.177 ppm) chloropicrin and allowed to equilibrate overnight. The next day a second XAD-4 tube was attached, and 10 liters humid air (89% RH) was pulled through them at 0.2 L/min. The tubes were opened, desorbed with ethyl acetate, and analyzed by GC-ECD. The retention efficiency averaged 97.5%. There was some chloropicrin found on the backup portions of the second tubes. (Table 2.4.2)

Table 2.4.2
Retention Study With 10 L

tube #	% recovery				total
	front tube		back tube		
	'A'	'B'	'A'	'B'	
1	86.1	9.6	3.3	0.2	99.2
2	76.9	13.8	6.4	0.5	97.6
3	82.9	10.5	3.2	0.2	96.8
4	77.4	12.7	5.8	0.5	96.4

overall average = 97.5%

2.5 Storage

Twelve tubes were spiked with 6.64 µg (0.198 ppm) chloropicrin and stored at room temperature until opened and analyzed. Six tubes were stored in the dark, and six tubes were stored under room lights. The recoveries averaged 98.3% for the dark samples stored for 14 days. The samples stored under room lights decreased to a 91.6% recovery when stored for 14 days. (Table 2.5)

Table 2.5
Storage Study

day	% recovery	
	light	dark
7	94.8	96.8
7	95.9	96.8
7	94.6	102
average	95.1	98.5
-----	-----	-----
14	91.5	99.8
14	93.4	98.4
14	89.9	96.4
average	91.6	98.2

overall average = 93.4% for light

overall average = 98.4% for dark

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.332, 1.66, 3.32, and 6.64 µg/mL chloropicrin in ethyl acetate with 0.04 µL/mL methylene chloride internal standard. The pooled coefficient of variation was 0.0134. (Table 2.6)

Table 2.6
Precision Study

injection number	0.322 µg/mL	1.66 µg/mL	3.32 µg/mL	3.34 µg/mL
1	80597	360994	693030	1355453
2	82315	358426	695874	1347293
3	79872	358399	696123	1351383
4	79852	358267	702018	1366389
5	84808	359793	700711	1379674
6	83235	359322	699542	1365029
average	81779	359200	697883	1360870
standard deviation	±2016	±1067	±3422	±11875
CV	0.0247	0.00297	0.00503	0.00873
pooled CV	0.0134			

Where:

$$CV \text{ (Coefficient of Variation)} = \frac{\text{standard deviation}}{\text{average}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

CV1, CV2, CV3, CV4 = Coefficient of Variation for each group.

A1, A2, A3, A4 = Number of injections at each level.

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 5 liters.

2.7.2 The sampling rate studied was 0.1 liters per minute. A maximum flow of 0.2 liters per minute may be used.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with an electron capture detector. A HP 5890 series II gas chromatograph was used in this study.

- 3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 60-m x 0.32-mm i.d. (1.0 μm d_f , RTX-5) capillary column.
 - 3.1.3 An electronic integrator or some other suitable method of measuring peak areas.
 - 3.1.4 Two-milliliter vials with PTFE-lined caps.
 - 3.1.5 A 1- μL syringe or other convenient size for sample injection.
 - 3.1.6 Pipettes for dispensing the desorbing solution.
 - 3.1.7 Volumetric flasks - 5 mL, and other convenient sizes for preparing standards.
- 3.2 Reagents
- 3.2.1 Purified GC grade nitrogen, hydrogen, and air.
 - 3.2.2 Chloropicrin Reagent grade
 - 3.2.3 Ethyl acetate, Reagent grade
 - 3.2.4 Methylene chloride, Reagent grade
 - 3.2.5 Desorbing solution of 0.04 $\mu\text{L}/\text{mL}$ methylene chloride in ethyl acetate. If methylene chloride is present in the workplace, do not use an internal standard.
- 3.3 Sample preparation
- 3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.
 - 3.3.2 Each section is desorbed with 1 mL of the desorbing solution.
 - 3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.
- 3.4 Standard preparation
- 3.4.1 Standards are prepared by diluting a known quantity of chloropicrin with the desorbing solution.
 - 3.4.2 At least two separate stock standards should be made.
 - 3.4.3 Dilutions of the stock standards are made to cover the range of the samples.
 - 3.4.4 A stock solution of 1.0 $\mu\text{L}/\text{mL}$ is 1.66 mg/mL, or 1.66 $\mu\text{g}/\mu\text{L}$. A dilution of 20- μL stock in 5 mL desorbing solution is 6.64 pg/mL. The range of standards used in this study was 0.166 to 6.64 $\mu\text{g}/\text{mL}$.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature (°C)</u>	
Nitrogen (make-up):	30	Injector:	140
Hydrogen (carrier):	1.5	Detector:	300
Hydrogen (detector):	30	Column:	100

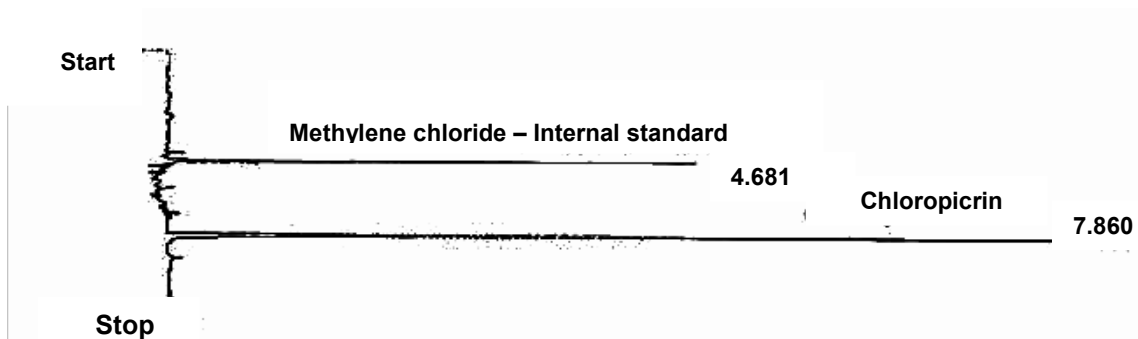


Figure 1. An analytical standard of 6.64 $\mu\text{g}/\text{mL}$ chloropicrin in ethyl acetate with 0.04 $\mu\text{L}/\text{mL}$ methylene chloride internal standard.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for the samples are plotted with the calibration curve to obtain the concentration of chloropicrin in solution.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume})}{(\text{desorption efficiency})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1 \text{ g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$

$$ppm = \frac{(volume\ of\ analyte)(10^6)^*}{(air\ vol,\ L)}$$

* All units must cancel

- 3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 5-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(5\ L)(DE)(MW)}$$

μ /mL = Concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25°C and 760 mmHg.
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
5 L = 5 Liter air sample
DE = Desorption efficiency
MW = 164.39

- 3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

- 3.8.1 All handling of solvents should be done in a hood.
3.8.2 Avoid skin contact with all chemicals.
3.8.3 Wear safety glasses, gloves and a lab coat at all times.

4 Recommendations for further study

A collection study should be performed.

5 References

- 5.1 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 333.
5.2 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists.