California Dept. of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
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Revision 2

Determination of Chloropicrin by GC/MS

1. Scope

   This method is for the analysis of Chloropicrin adsorbed onto XAD-4 in air sampling tubes by GC/MS and is to be followed by all authorized Environmental Monitoring personnel. The reporting limit of Chloropicrin is 0.025 µg per sample.

2. Principle

   Chloropicrin (Cl_3CNO_2) in the air is adsorbed onto XAD-4 resin in air sampling tubes, desorbed from the resin with methylene chloride and subsequently analyzed by GC/MS.

3. Safety

   3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.
   3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

4. Interferences

   There were no known matrix interferences that caused qualitative or quantitative problems at the time of validation.

5. Apparatus and Equipment

   5.1 Test Tubes, 25 mL, with Teflon-lined screw caps
   5.2 Test Tube Rack
   5.3 Disposable Pasteur pipettes and any miscellaneous glassware as needed
   5.4 Micro Syringes
   5.5 Filters, Nylon Acrodisc, 0.45 µm, Gelman Sciences
   5.6 Volumetric Flasks
   5.7 File capable of scoring the glass sampling tube or a Dremel (an electric rotary flex shaft tool) with a ¾ inch diamond saw
   5.8 Forceps
   5.9 Box Cutter or razor blade
   5.10 Fisher Vortex Genie 2, or equivalent
   5.11 Branson 5800 Sonicator, or equivalent
   5.12 Automated Pipette or Volumetric Pipette, 5 mL
   5.13 Autosampler Vial, 2 mL, with caps
   5.14 Electronic crimper

5.15 Agilent Technologies Gas Chromatograph GC (7890A) with Agilent Technologies Mass Detector MSD (5975C inert XL) or equivalent.

6. Reagents and Supplies

6.1 Methylene chloride, nanograde or equivalent pesticide grade
6.2 Standard: 1.0 mg/mL reference standard of Chloropicrin (CAS No. 76-06-2).
6.3 XAD-4 Air Sampling Tube, SKC 226-175
6.4 Filters, Nylon Acrodisc, 0.45µm, Gelman Sciences or equivalent.

7. Standards Preparation

7.1 Standards are ordered from an ISO 17034 accredited vendor.
7.2 Dilute the 1.0 mg/mL Chloropicrin standard with methylene chloride to the following working standard concentrations: 0.0025 ng/µL, 0.01 ng/µL, 0.025 ng/µL, 0.05 ng/µL, 0.1 ng/µL, 0.25 ng/µL, and 0.5 ng/µL
7.3 Store all standards in the appropriately designated freezer
7.4 The expiration date of each standard is six months after the preparation date.

8. Sample Preservation and Storage

All samples to be extracted are to be stored in the designated freezer and all sample extracts are to be stored in the designated refrigerator (4 ± 3°C).

9. Test Sample Preparation

9.1 Sample Preparation

9.1.1 Remove the samples from the freezer and place them in the fume hood to allow the samples to warm to ambient temperature.
9.1.2 Fold a piece of white printer paper into quarters, open the folded paper, and place it under where the samples are going to be handled to catch any spilled XAD-4 resin.
9.1.3 Using an automated pipette or a 5 mL volumetric pipette, transfer 5 mL of methylene chloride into a 25 mL test tube and cap the tube to prevent solvent evaporation.
9.1.4 Score the sampling tube with a file or Dremel just above the top glass wool layer of the sampling tube.
9.1.5 Break the sampling tube by holding the sampling tube horizontally in both hands with your thumbs on opposite sides of the score mark, with the score mark facing away from you, and applying steady pressure until the tube breaks.

9.1.6 Remove the top glass wool layer with forceps and place it in the test tube containing the methylene chloride and pour the first segment of resin into the sampling tube. Resin that is adhered to the side walls of the sampling tube may be removed by inverting the sampling tube in the test tube and tapping the side of the sampling tube with the forceps.

9.1.7 Repeat steps 9.1.4 to 9.1.6 for the second section of the sampling tube.

9.1.8 Remove the rubber end cap of the sampling tube with a box cutter or razor blade by cutting vertically down the sampling tube, slicing the rubber cap so that it is easily removed.

9.1.9 Invert the remaining sampling tube section into the test tube, and using a 9-inch disposable pipette, push the last section of glass wool into the test tube.

9.1.10 Immediately cap the test tube and vortex to get all of the resin and glass wool into the solvent.

9.1.11 Place the test tube in a test tube rack and place the test tube rack in the Sonicator with the water level above the solvent line in the test tube. Sonicate the sample for 10 minutes.

9.1.12 Remove the sample from the Sonicator and filter through a micro syringe fitted with a 0.45 µm Nylon Acrodisc into an autosampler vial and cap immediately for GC/MS analysis.

9.2 Quality Control Sample Preparation

9.2.1 Blank Preparation

9.2.1.1 Break both ends of a blank SKC 226-175 sample tube and follow Sample Preparation steps 9.1.6 to 9.1.12.

9.2.2 Spike Preparation

9.2.2.1 Break both ends of a blank SKC 226-175 sample tube and use a syringe to inject a known amount of Chloropicrin into the large resin section of the tube and follow Sample Preparation steps 9.1.6 to 9.1.12.

10. Instrument Calibration

10.1 The recommended concentrations of the standards used to establish the calibration curve were 0.0025 ng/µL, 0.01 ng/µL, 0.025 ng/µL, 0.05 ng/µL, 0.1 ng/µL, 0.25 ng/µL, and 0.5 ng/µL.

10.2 The calibration standards are fitted with linear regression or a quadratic fit with a correlation coefficient, $r \geq 0.995$ or a coefficient of determination, $r^2 \geq 0.990$.

11. Analysis

11.1 Injection Scheme

The recommended injection scheme is as follows:
Set of Calibration Standards, Solvent Blank, Matrix Blank, Matrix Spike, Solvent Blank, Samples, Solvent Blank, Set of Calibration Standards, Solvent Blank, Matrix Blank, Matrix Spike, Solvent Blank, Samples, Solvent Blank, Set of Standards

11.2 Instrumentation and Operating Conditions

11.2.1Agilent Technologies Gas Chromatograph Model 7890A with Agilent Technologies Mass Detector Model 5975C MSD

Column: Restek: Rtx-200, 60m x 0.32mmID x 0.5 µm df
Gas Flow: Carrier Gas, Constant Pressure (Helium), 20 psi
Injection-Type: Pulsed Splitless Injection, 50 psi
Injector Temperature: 140 °C
Injection Volume: 2.0 µL

Oven Temperature Program				
	Rate (°C/min)	Value (°C)	Hold Time	Run Time
Initial		40	0	0
Ramp 1	10	150	0	11
Ramp 2	35	280	0	14.714

Retention Time: 8.2 min

Mass Spectrometer Parameters
Transfer Line Heater: 160
MS Source Temperature: 160
MS Quad Temperature: 150
Dwell Time: 1 min
Selected Ions: 121, 119, 117, 82

12 Quality Control

12.1 A seven-point calibration curve of 0.0025 ng/µL, 0.01 ng/µL, 0.025 ng/µL, 0.05 ng/µL, 0.1 ng/µL, 0.25 ng/µL, and 0.5 ng/µL are obtained at the beginning and end of each set of samples for calculating the response factor as well as monitoring instrument performance throughout a sample list.

12.2 Each set of samples will be limited to 20 samples or less per batch and will have at least one matrix blank and matrix spike per sample batch.

12.3 The matrix blank will be free of any chloropicrin at or above the

reporting Limit.

12.4 The recovery of the matrix spike will be within the Control Limits.

12.5 The retention time will be within 0.1 minute of the corresponding standard.

12.6 The sample must be diluted if the initial results fall outside the linear range of the standard curve.

12.7 Bracketing standard response will have equal to or less than a 20% change.

12.8 Method Detection Limit (MDL)

The method detection limit refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 replicate SKC 226-175 XAD-4 resin sampling tubes were spiked with 0.01 µg/mL Chloropicrin solution. The standard deviation of the results of the spiked samples are used to calculate the MDL using the following equation:

$$MDL = tS$$

Where t is the Student t-test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For n=7 replicate samples used to determine the MDL, t= 3.143.

Method Detection Limit (MDL) Data Results are in Appendix I.

12.9 Reporting Limit (RL)

The 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 reporting limit (RL). Per client agreement, the RL is chosen to be in a range 1 – 5 times the MDL, unless otherwise agreed upon by the client.

12.10 Method Validation Recovery Data and Control Limits

12.10.1 The method validation consisted of five sample sets with each set consisting of a matrix blank and five fortification levels as follows: 0.1, 0.25, 0.5, 1.0, and 2.5 µg/ sample. A reagent blank will be included when a new lot of solvent is used for extraction. All spikes, method blanks, and reagent blank samples were processed through the entire analytical method.

12.10.2 Upper and Lower Warning and Control Limits are set at ± 2 and ± 3 the standard deviation of the percent average recovery, respectively.

Method Validation Data Results are in Appendix II

13 Calculations

13.2 The quantitation is based on the area counts of the target compound. The calculations are based on external standards (ESTD) and are linear fit.

13.3 The correlation coefficient, slope, and intercept of the linear regression line are calculated once the calibration standards are defined. The equation for calculating the analyte of interest is as follows:

$$y = mx + b$$

Where, y = peak response
m = slope
b = intercept
x = concentration of analyte

When the unit and the dilution factor are entered into the instrument correctly before doing analysis, the software will correctly generate the results.

13.4 Results for any sample can be manually calculated with a single point standard resulting in the final units of µg per sample. This calculation can be used to verify any results obtained from the instrument. The equation is as follows:

$$\mu g = \frac{\text{(Sample peak area) (std. conc. ng/µL) (std. vol. injected) (Sample final vol., (mL))(1000 µL/mL)}}{\text{(Std. peak area) (Sample vol. injected) (1000ng/µg)}}$$

14 Acceptance Criteria

14.1The peak retention between standards, quality control spikes, and unknown samples must be within 5 seconds. If there is an unknown reason for a shift in retention time, an explanation memo must be included.

14.2 Peak response must be within the calibration range.

14.3 The r^2 of the calibration curve or overlay calibration curves must be greater than 0.990.

14.4 Quality control spikes must be within the established control range, otherwise they will be repeated.

14.5 The sample shall be diluted if the results exceed the response of the highest calibration standard in the curve or up to 30% higher than the highest calibration response when using a single point calculation

14.6 The recoveries of the matrix spike shall be within the control limits.

14.7 When the spike recoveries fall outside the control limits, the analyst must investigate the cause. The entire extraction set of samples is re-analyzed. If the recoveries fall within the control limits the results will be reported.

15 Reporting

15.2 Sample results are reported according to the client's analytical laboratory specification sheet.

15.3 The Chain of Custody, Quality Control sheet, and Control Chart are to be completed and presented in the data package.
15.4 The data package is to be prepared, peer reviewed, and reported.

16 Discussion

16.2 This method is a second revision to the original EM16.0 method.
16.3 The following modifications have been implemented:
Method transferred to GC/MS
New Restek column fitted
Extraction Changes: Changed solvent to methylene chloride, added the sonicator, and added Nylon Acrodisc.

17 References

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

Appendix I: Method Detection Limit

10 ng/sample of Chloropicrin was used for each spike

Sample	Injection 1 (ng/sample)	Injection 2 (ng/sample)	Average (ng/sample)

Appendix I: Method Detection Limit

10 ng/sample of Chloropicrin was used for each spike

Sample	Injection 1 (ng/sample)	Injection 2 (ng/sample)	Average (ng/sample)
Blank	ND	ND	ND
Spike 1	6.86	6.56	6.71
Spike 2	8.10	7.92	8.01
Spike 3	6.62	7.59	7.11
Spike 4	8.22	7.75	7.99
Spike 5	10.94	11.49	11.22
Spike 6	6.99	9.31	8.15
Spike 7	8.34	8.96	8.65

*:ND = Not Detectable

Standard Deviation: 0.00146
Method Detection Limit (MDL): 0.00458 µg/sample

Appendix II: Method Validation

Sample	Day 1	Day 2	Day 3	Day 4	Day 5
Blank	ND	ND	ND	ND	ND
0.1 µg SPK	106.83	110.75	89.24	87.32	92.56
0.25 µg SPK	101.56	108.86	92.66	102.90	99.22
0.5 µg SPK	108.29	114.26	103.81	111.61	100.70
1.0 µg SPK	103.93	112.90	111.26	77.24	90.52
2.5 µg SPK	68.67	100.36	106.94	74.41	94.17

*ND = Not Detectable

Average	**98.84**
Standard Deviation	**12.35**
Upper Control Limit (UCL)	**135.89**
Lower Control Limit (LCL)	**61.78**
Upper Working Limit (UWL)	**123.54**
Lower Working Limit (LWL)	**74.14**

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Revision Log:

Date	What was revised? Why?
6/9/14	Added in new validation results to lower the reporting limit (RL) to 0.05 µg/tube.
7/8/20	Transferred method to GC/MS. Completed new MDL and validation. Lowered Reporting Limit (RL) to 0.025 µg/tube. Updated extraction procedure to use a different solvent, sonicator, micro syringe, and Nylon Acrodisc filter.