Standard Operating Procedure for the Analysis of Trichloronitromethane (Chloropicrin) In Ambient Air Using Gas Chromatography/Mass Spectrometry

MLD075
Revision 1.0

Northern Laboratory Branch
Monitoring and Laboratory Division

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Standard Operating Procedure
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1. Scope

This standard operating procedure describes the determination of trichloronitromethane (chloropicrin) in ambient air samples using a gas chromatograph/mass spectrometer (GC/MS) or gas chromatograph/triple quadrupole mass spectrometer (GC/MS/MS). The procedure is for the analysis of chloropicrin collected on XAD-4 sorbent tubes. This Standard Operating Procedure (SOP) is used in conjunction with the Northern Laboratory Branch (NLB) Laboratory Quality Control Manual (QCM).

2. Summary of Method

Air samples are collected on 600 milligrams of XAD-4 in glass sorbent tubes. The samples are stored at or below 5 degrees Celsius (°C) until extracted with 4.0 mL of pesticide grade ethyl acetate. The extract is analyzed by a GC/MS with a split/splitless inlet in the selected ion monitoring (SIM) mode. Alternatively, a GC/MS/MS with a Programmable Temperature Vaporizing (PTV) inlet in the selected reaction monitoring (SRM) mode may be used. Sample analysis and quantitation uses an external standard method for instrument calibration.

3. Acronyms

Acronym or Term	Definition
ºC	Degrees Celsius
CARB	California Air Resources Board
CCV	Continuing Calibration Verification
CS	Control Standard
DPR	Department of Pesticide Regulation
EI	Electron Ionization
EQL	Estimated Quantitation Limit
GC/MS	Gas Chromatography/Mass Spectrometry
GC/MS/MS	Gas Chromatograph/Triple Quadrupole Mass Spectrometer
LCS	Laboratory Control Spike
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation

Acronym or Term	Definition
m	Meter
MDL	Method Detection Limit
mg/mL	Milligrams per Milliliter
MLD	Monitoring and Laboratory Division
mm	Millimeter
ng/mL	Nanograms per Milliliter
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
PFTBA	Perfluorotributylamine
PS	Chloropicrin (military designation)
PTV	Programmable Temperature Vaporizing
QC	Quality Control
QCM	Quality Control Manual
RPD	Relative Percent Difference
SDS	Safety Data Sheet
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SRM	Selected Reaction Monitoring
µg	Microgram
UHP	Ultra-High Purity
µm	Micrometer

4. Definitions

4.1. ANALYTICAL BATCH – A set of prepared samples (i.e., extracts) analyzed together as a group in an uninterrupted sequence.

4.2. BLANK – Sample media, solvent, or reagent that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, and/or analysis. The blank is subjected to the same analytical processes as samples.

4.2.1. METHOD BLANK – An XAD-4 sorbent tube that is free of analytes of interest. The sorbent tube is extracted in the same manner and at the same time as samples and is taken through the entire sample analysis process. It is used to monitor the laboratory preparation and analysis systems for interferences and contamination.

4.2.2. SOLVENT BLANK – An aliquot of solvent analyzed with each batch of samples to indicate any contamination or artifacts that may come from the reagents and analytical steps.

4.2.3. FIELD BLANK – An XAD-4 sorbent tube that goes out to the field

and is treated as a sample where it will be connected to a sampler, disconnected without pulling an air sample, then returned to the laboratory. Field blanks are treated like samples in the laboratory. The field blank identifies any potential contamination that may occur from ambient conditions, sample handling, or other sources that samples may be exposed to.

4.2.4. TRIP BLANK – An unopened XAD-4 sorbent tube which travels to the field and then back to the laboratory. Trip blanks are treated like samples in the laboratory. The trip blank may aid in identifying any potential issues arising through transportation which could affect the sorbent.

4.3. BREAKTHROUGH – Breakthrough occurs when analytes of interest migrate through the XAD-4 sorbent tube from the primary sorbent bed to the secondary sorbent bed.

4.4. BREAKTHROUGH ANALYSIS – Breakthrough analysis refers to analysis of the secondary sorbent bed of the XAD-4 sorbent tube to determine if any amount of sample was not retained in the primary sorbent bed. One breakthrough analysis is done per every ten samples, at a minimum. Breakthrough analysis is also done for any samples which exceed the breakthrough threshold limit.

4.5. BREAKTHROUGH THRESHOLD LIMIT – The concentration found in the primary sorbent bed that would require analysis of the secondary sorbent bed. The breakthrough threshold limit is set at > 500 ng/mL. Therefore, detections at over 500 ng/mL require analysis of the secondary sorbent bed to check for breakthrough.

4.6. CALIBRATION CURVE – The graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response.

4.7. CARRYOVER – Contamination from an adjacent sample causing false or inaccurate results in the subsequent sample(s).

4.8. CARRYOVER CHECK – A blank which is analyzed after a high concentration sample to determine if any carryover may have occurred.

4.9. COLLOCATED SAMPLE – A sample used to assess total precision (sampling and analysis) which is located within a specified radius of the primary sampler. The collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.

4.10. CONTINUING CALIBRATION VERIFICATION (CCV) – A midpoint calibration standard analyzed, at a minimum, once per every ten samples and at the end of the analytical batch to confirm the stability of the instrument calibration.

4.11. CONTROL STANDARD (CS) – A midpoint standard analyzed after the calibration curve. The CS should be prepared with a stock standard that is different from what was used to prepare the calibration standard, when available. The CS must be analyzed at a minimum of once per analytical batch.

4.12. DILUTION – Dilution is the process of reducing the concentration of a solute in solution, usually by adding more solvent. Dilutions are required when any sample concentration exceeds the calibrated linear range by more than ten percent. After diluting, the concentration should fall within the calibrated linear range. Multiple dilutions are sometimes necessary.

4.13. ESTIMATED QUANTITATION LIMIT (EQL) – The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally five to ten times the MDL. The EQL may be used as the reporting limit if requested by the client.

4.14. EXTRACTION BATCH - A batch of samples and associated quality control (QC) which are taken through the extraction process together. The extraction batch is typically analyzed in one analytical batch.

4.15. HOLD TIME – The maximum amount of time a sample or extract may be stored prior to performing an operation. Extraction hold time is from sample collection to extracting the sample. Analytical hold time is from sample extraction to analysis.

4.16. INTERFERENCE – Discrete artifacts or elevated baselines from solvents, reagents, glassware, and other sample processing hardware that may cause misinterpretation of the chromatographic data. Other interferences include matrix effects, which may cause the target compound to recover higher or lower than the expected value.

4.17. METHOD DETECTION LIMIT (MDL) – A statistically derived value that is defined as being the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sample media) containing the analyte. The procedure used to determine the MDL is documented in the NLB's Quality Control Manual.

4.18. REPLICATE – A second analysis of a randomly chosen sample within an analytical batch.

4.19. REPORTING LIMIT (RL) – A value that is equivalent to or greater than the limit of quantitation. Detections below the reporting limit are typically reported as "< RL" unless otherwise requested by the client.

4.20. SPIKE – A known concentration of a standard containing target analytes is added to sampling media or reagent. Spike recoveries indicate efficiency of laboratory or field procedures.

4.20.1. FIELD SPIKE – An XAD-4 sorbent tube is spiked with a known concentration of target analyte that goes out to the field and is treated as a sample, where it will be connected to a collocated sampler and sampled as normal to check for matrix effects. The unspiked collocated sample results are subtracted from the field spike results to determine field spike percent recovery.

4.20.2. LABORATORY CONTROL SPIKE (LCS) – An XAD-4 sorbent tube is spiked with a known concentration of target analyte that is prepared, extracted, and analyzed with and in the same manner as samples. LCS recoveries indicate extraction efficiency.

4.20.3. TRIP SPIKE – An XAD-4 sorbent tube is spiked with a known concentration of target analyte, shipped along with sampling media, and is taken into the field, but returned unopened to the laboratory. Trip spike recoveries indicate if samples may have been affected by shipping conditions.

5. Interferences and Limitations

5.1. Interferences may be caused by contaminants in the filters, sampling media, solvents, sample extraction apparatus, filtration apparatus, and glassware. A method blank is extracted and analyzed with each set of samples to monitor these possible sources of contamination.

5.2. The analytical system may become contaminated when samples containing high compound concentrations are analyzed. If there is suspected carryover from a high concentration sample, the succeeding sample(s) is reanalyzed to verify results.

5.3. High boiling point compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous "ghost" peaks. The column should be baked out to remove these contaminants prior to analyzing samples. The bake out temperature must not exceed the column's maximum operating temperature.

6. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with detailed knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and Laboratory Information Management System (LIMS) functionality pertaining to the program.

Personnel will provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

Training will be documented and maintained by the laboratory supervisor.

7. Safety Requirements

All personnel must follow the general health and safety requirements found in Northern Laboratory Branch's (NLB) Chemical Hygiene Plan.

Chloropicrin is used in agriculture as a soil fumigant. It has also been used as a chemical warfare agent (military designation is PS) and a riot control agent. Chloropicrin is an irritant with characteristics of a tear gas and has an intensely irritating odor. Inhalation of 1 part per million (ppm) causes eye irritation and can warn of exposure. The analyst should refer to the safety data sheets (SDS) for additional information regarding chemical properties and precautions.

The handling and preparation of samples, extracts, and standards must be conducted in a hood. Proper personal protective equipment must be worn, including neoprene or nitrile gloves, safety glasses, and a laboratory safety coat. Analysts should ensure that engineering and air quality controls are active and operating properly to reduce or eliminate off-gassing from instrument exhaust ports.

This method uses high pressure gases. Refer to safe handling practices regarding compressed gases when moving and installing the cylinders.

The GC and MS have heated zones which may cause burns. Avoid contact with these zones and devices when in operation and make certain they are de-energized and at ambient temperature prior to servicing.

8. Hazardous Waste

As chloropicrin waste is categorized as acutely toxic, the waste must be disposed of within 90 calendar days upon accumulation of 1.0 kg. The NLB Health &

Safety Coordinator should be notified upon accumulation of 1.0 kg (approximately two pounds) of this waste. Waste consists of liquid chloropicrin and unanalyzed XAD-4 sorbent tubes used to capture chloropicrin. Chloropicrin waste should be stored in the waste containers provided for this purpose. The containers should be properly labeled with appropriate hazardous waste labels indicating the contents and start date of accumulation.

9. Equipment and Supplies

9.1. Gas Chromatograph: system with programmable oven, electronic pressure control for capillary columns, heated injector, and automated liquid injector

9.2. Column: Restek Rtx-200, 60 meter, 320 µm inner diameter, 0.5 µm film thickness, or equivalent. For GC/MS/MS analysis, a Thermo Fisher TG-5SILMS 30 m x 0.25 mm x 0.25 µm column (or equivalent) may be used

9.3. Detector: single quadrupole Mass Selective Detector or triple quadrupole Mass Selective Detector

9.4. XAD-4 sorbent tubes: 600/200 mg custom tube, SKC. Two 400/200 mg XAD-4 tubes such as SKC, Incorporated (catalog # 226-175) may be used in tandem if the custom tube is not available

9.5. Syringe Filters: Disposable PTFE 0.2 µm filter, such as VWR Cat. No. 28145-491

9.6. Disposable Syringes: such as BD disposable syringes (part # 309656) 3 – 5 mL volume

9.7. 4 mL glass storage vials with Teflon lined screw caps such as VWR (part # 66009-876)

9.8. Screw-cap test tubes, such as Globe Scientific part # 89497-770

9.9. Ultrasonic bath: capable of temperature programing such as Branson model 8510

9.10. 8 mL glass extraction vials such as Kimble Chase (part # 60940A-8)

9.11. Autosampler deactivated vials with cap such as National Kit 100-pack (part # CERT5000-82W)

9.12. Auto sampler flat bottom inserts such as VWR 0.4 mL 1000-pack (Cat. No. 82028-454)

9.13. 25 mL volumetric flasks

9.14. Analytical balance capable of weighing as low as 0.1 mg

9.15. Eppendorf electronic pipettes: 100-5000 µL volume ranges

9.16. Disposable Pasteur pipettes: 5 ¾" such as Duran Wheaton Kimble (part # 63A54)

9.17. Tweezers

9.18. Hand-held glass cutter

9.19. Disposable nitrile or neoprene gloves to handle organic solvents

9.20. Hamilton microliter syringes (or equivalent): 10 µL, 50 µL, and 250 µL volume ranges

9.21. Refrigerator/freezer capable of maintaining a consistent temperature at or below 5°C

10. Reagents

10.1. Ethyl acetate solvent, pesticide grade or better, CAS No 141-78-6

10.2. Chloropicrin, such as Chem Service, 98.8 percent (part # N-11452-1G, neat standard)

10.3. Perfluorotributylamine (PFTBA) tune solution

10.4. Helium Ultra-High Purity (UHP), 99.999 percent for use as the GC column carrier gas

10.5. Argon, (UHP), 99.999 percent for use with the triple quadrupole MS

11. Standards Preparation

All standard solutions are prepared using ethyl acetate (pesticide grade or better) as the solvent. The solutions are stored at or below 5°C until used. Standard solutions are equilibrated to room temperature before use, and returned to cold storage at the end of the work day.

Neat standards and standards purchased in solution are valid up to the manufacturer's expiration date. Working standards expire one year from preparation date, but are not to exceed the expiration date of the neat or parent solution. Standard preparation is documented in a logbook.

11.1. Calibration Standards

11.1.1. A 1.0 mg/mL chloropicrin stock standard is prepared by weighing out approximately 0.025 g neat chloropicrin in a 25 mL volumetric flask and filling to volume with ethyl acetate.

Intermediate A, a 50,000 ng/mL intermediate standard, is made using a 1.25 mL aliquot of the 1.0 mg/mL stock solution in a 25 mL volumetric flask and filling to volume with ethyl acetate. Intermediate B, a 5,000 ng/mL intermediate standard, is made using a 2.5 mL aliquot of Intermediate A in a 25 mL volumetric flask and filling to volume with ethyl acetate. Intermediate C, a 500 ng/mL standard, is made using a 2.5 mL aliquot of Intermediate B in a 25 mL volumetric flask. Volumes may be adjusted to accommodate for the concentration of the stock standard solution and/or if smaller volumetric flasks are used. See Table 1 for a summary.

Table 1. Chloropicrin Stock and Intermediate Standards Preparation

Stock Standard (ng/mL)	Amount	Final Volume (mL)	Final Concentration
Stock	0.025 g neat	25	1.0 mg/mL
Intermediate A	1.25 mL of stock	25	50,000 ng/mL
Intermediate B	2.5 mL of Intermediate A	25	5,000 ng/mL
Intermediate C	2.5 mL of Intermediate B	25	500 ng/mL

11.1.2. Calibration standards: Table 2 lists calibration curve standard preparation. Five calibration levels ranging from 2 ng/mL to 500 ng/mL is recommended. These standards are made by spiking aliquots of intermediate standard solution onto XAD-4 sorbent tubes. The tubes are extracted with 4.0 mL of ethyl acetate and sonicated at ambient temperature for one hour. The extracts are filtered and stored at or below 5°C.

Table 2. Chloropicrin Calibration Standard Preparation

Calibration Level	Standard	Spike Amount (µL)	Extraction Volume (mL)	Final Concentration (ng/mL)
1	Intermediate C	16	4	2
2	Intermediate B	8	4	10
3	Intermediate B	40	4	50
4	Intermediate A	8	4	100
5	Intermediate A	40	4	500

11.2. Control Standard (CS)

A mid-level chloropicrin control standard is prepared in the same manner as described in section 11.1, using a second source standard. If a neat standard is used to make the CS, preparation may follow this scheme: prepare a 1.0 mg/mL CS stock in the same manner as described in section 11.1.1, using a second source standard. A 10,000 ng/mL CS intermediate is prepared by diluting 0.25 mL of CS stock to 25 mL in a volumetric flask, using ethyl acetate as the diluent.

If a chloropicrin standard purchased in solution (such as ChemService item # S-11452B1-1mL, 100 µg/mL) is used as the second source, prepare a CS intermediate at 8,000 – 10,000 ng/mL, using ethyl acetate as the diluent. Preparation may follow this scheme: add 0.20 mL of 100 µg/mL chloropicrin solution to a 2.0 mL volumetric flask and bring to volume for a final concentration of 10,000 ng/mL, using ethyl acetate as the diluent.

A mid-level working CS (40 – 60 ng/mL) is prepared from the intermediate CS standard by spiking the appropriate amount onto an XAD-4 sorbent tube. The tube is extracted with 4.0 mL of ethyl acetate and sonicated at ambient temperature for one hour. The extract is filtered and stored at or below 5°C.

A CS is analyzed after the 5-point calibration curve. The CS criteria are based on established control limits.

11.3. Laboratory Control Spike (LCS)

A spiked 30 ng/mL LCS is prepared by spiking 24 µL of Intermediate B onto an XAD-4 sorbent tube. The tube is extracted with 4.0 mL of ethyl acetate and sonicated at ambient temperature for one hour. The extract is filtered and stored at or below 5°C. One LCS is to be extracted and analyzed with every extraction batch.

11.4. Field Spikes and Trip Spikes

Prepare the appropriate number of field spikes and trip spikes, as required by field sampling protocol, by spiking 24 µL of Intermediate B onto each XAD-4 sorbent tube. Properly label the XAD-4 sorbent tubes with the date, time, and description (either “field spike” or “trip spike”). Spiked tubes are placed in individual screw-top test tubes and stored at or below 5°C.

12. Media and Sample Storage

12.1. Media Storage – Prior to sampling, unopened XAD-4 tubes are stored and shipped at ambient temperature.

12.2. Spiked Field QC Storage - Spiked XAD-4 field QC tubes (field spikes, trip spikes) are stored at or below 5°C prior to sampling.

12.3. XAD-4 Sample Storage – After sampling, all XAD-4 tubes are stored at or below 5°C until extraction.

12.4. Extract Storage – After extraction, all extracts are stored at or below 5°C.

13. Sample Extraction and Analysis

All samples (primary and secondary sorbent beds) are extracted with 4 mL of ethyl acetate (pesticide grade or better).

13.1. Sample Preparation and Extraction

13.1.1. Prior to sample analysis, remove the samples from cold storage and allow them to equilibrate to room temperature. Samples must be extracted within 28 days of collection.

13.1.2. Obtain the necessary amount of 8 mL glass vials (one for each XAD-4 sorbent tube) and put them on a sampling tray. Label each one clearly with the appropriate standard or sample IDs for each sample.

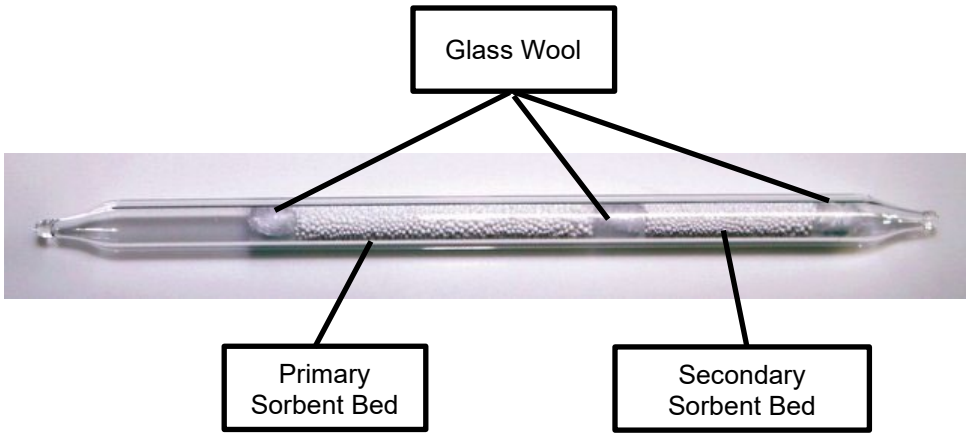
13.1.3. The custom XAD-4 sorbent tube is comprised of two sections separated by glass wool. The longer end (primary sorbent bed) contains 600 mg of XAD-4. It is used for sample analysis. The short end (secondary sorbent bed) contains 200 mg of XAD-4 and is used to test for sample breakthrough. One breakthrough (secondary sorbent bed) analysis should be done for every ten samples, at a minimum.

If custom 600/200 mg XAD-4 tubes are not available, 400/200 mg

tubes can be used. The XAD-4 400/200 tube is comprised of two sections separated by glass wool. The longer end contains 400 mg of XAD-4, and the shorter end contains 200 mg. 600 mg of XAD-4 is needed to trap chloropicrin when sampled at 24 hours using a flow rate of 0.1 L/min; therefore, both sections of the tube must be used to contain the sample. For breakthrough monitoring, a second XAD tube must be used in tandem with the primary tube.

13.1.4. Remove the XAD-4 sorbent tube from the screw-top container. Remove the red cap from the end of the primary sorbent bed. Remove the glass wool plug using tweezers. If any of the glass wool contains XAD-4 sorbent, shake off the XAD-4 sorbent into the vial. The glass wool itself can be added to the vial if XAD-4 adheres to the wool. See Figure 1.

Figure 1. XAD Sorbent Tube



13.1.5. Pour the XAD-4 sorbent from the primary sorbent bed into its correspondingly labeled 8 mL glass vial.

13.1.6. Score the tube with the glass cutter just in front of the second section of glass wool and carefully break the tube. Using an automatic pipette, rinse the empty primary sorbent bed of the cut-off tube with 4 mL of ethyl acetate collecting the solvent in the 8 mL glass vial. Retain the secondary sorbent bed for breakthrough analysis, if needed.

13.1.7. If 400/200 mg XAD-4 tubes were used, then the 200 mg portion of the tube must be combined with the 400 mg section. Remove the glass wool dividing the 200 mg section of XAD and pour the XAD sorbent from the secondary sorbent bed into the 8 mL glass vial. Remove the final glass wool plug from the tube. Using an

automatic pipette, rinse the empty tube with 4 mL of ethyl acetate, collecting the solvent in the 8 mL glass vial.

13.1.8. Cap the vial securely.

13.1.9. If breakthrough analysis is being done, extract the breakthrough sorbent bed as described in sections 13.1.4 – 13.1.8 as a separate sample, using 4 mL of ethyl acetate. The breakthrough sorbent bed is either the 200 mg section of the custom tube, or the primary (400 mg section) sorbent bed of the tandem tube. Shake off any sorbent remaining in the glass wool into the 8 mL vial.

13.1.10. Prepare a method blank with every extraction batch by opening an unused, clean XAD-4 sorbent tube.

13.1.11. Prepare a LCS with every extraction batch by opening an unused, clean XAD-4 sorbent tube and spiking the XAD-4 sorbent with 24 µL of Intermediate B onto the primary sorbent bed.

13.1.12. Repeat steps 13.1.3 through 13.1.8 for the LCS, method blank, applicable field QC, and all samples scheduled for analysis.

13.1.13. Fill ultrasonic bath to fill line with water. Place all vials containing extracts in the bath and sonicate for one hour at ambient temperature.

13.1.14. Filter each extract into individual 4 mL glass vials using a disposable syringe and a disposable 0.20 µm syringe filter. Label each one clearly with the standard names and preparation dates for each sample.

13.1.15. Transfer approximately 250 µL of each extract into individual 1.5 mL auto sampler vials equipped with a 250 µL insert.

13.1.16. Randomly choose one sample extract as a replicate to be analyzed a second time. One replicate must be analyzed for every ten samples, at a minimum.

13.1.17. Transfer approximately 250 µL of the calibration standards and control standard into individual 1.5 mL auto sampler vials equipped with a 250 µL insert. The extracts and standards are now ready for analysis. If extracts cannot be analyzed on the day of extraction, store the extracts at or below 5°C.

13.1.18. All extracted samples must be analyzed within 60 calendar days

of extraction.

13.2. Sample Analysis

13.2.1. Analytical Sequence

Each analytical run of ten or fewer samples must include bracketing standards, controls, replicates, and blanks as listed below. A 1.5 µL injection volume is used for all analyses. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Solvent blank
- Laboratory Control Spike
- Method Blank
- Samples (up to ten including breakthrough samples)
- Breakthrough analysis (one every ten or fewer samples)
- Replicate (one every ten or fewer samples)
- Solvent blank
- CCV (midpoint calibration standard)

13.2.2. Analytical Instrument Conditions

13.2.2.1 Single Quadrupole GC/MS with Split/Splitless Inlet
GC:

- Injection port temperature: 200°C
- Splitless injection: split flow 50 mL/min, splitless time 1.0 min
- Purge flow: 5.0 mL/min, constant septum purge
- Vacuum compensation: on
- Gas saver flow: 5 mL/min
- Gas saver time: 2 min
- GC Temperature Program:
  Oven initial 60°C, hold 1 min
  Ramp to 130°C at 15°C/min
  Ramp to 250°C at 35°C/min
  Run time = 10 min
- Column Flow: Helium, constant flow at 2.38 mL/min
- Chloropicrin retention time (approximate): 4.58 min

MS:

- Mass Spectrometer: Electron Ionization Single Quadrupole
- MS transfer line temperature: 245°C

- Ion source temperature: 250°C
- Selective Ion Monitoring: chloropicrin: 116.9 (quantitation ion), 118.9, 120.9 (qualitative ions)

13.2.2.2 Triple Quadrupole GC/MS/MS with Programmable Temperature Vaporizing (PTV) Inlet
GC:

- Splitless injection: split flow 26 mL/min, splitless time 1 min
- Purge flow: 5 mL/min, constant septum purge
- Vacuum compensation: on
- Gas saver flow: 5 mL/min
- Gas saver time: 2 min
- PTV inlet initial temperature: 70°C, hold 0.05 min
- Transfer: 14.5° C/s to 220°C, hold 0.05 min
- Cleaning: ramp at 14.5°C/s to 275°C, hold for 5min at 75 mL/min flow
- GC Temperature Program:
  Oven initial 40°C, hold for 0.5 min
  Ramp to 110°C at 15°C/min
  Ramp to 250°C at 35°C/min
  Run time: 10 min
- Column Flow: Helium, constant flow at 1.5 mL/min
- Chloropicrin retention time (approximate): 4.56 min

MS:

- Mass Spectrometer: Electron Ionization Triple Quadrupole
- MS transfer line temperature: 245°C
- Ion source temperature: 250°C
- Selective Reaction Monitoring (SRM): chloropicrin 116.9 – 81.9 (quantitation ion), 118.9 – 83.9 (qualitative ion)
- Collision energy: 26

Instrument tuning is done using the software parameters detailed on the Dashboard screen. Table 3 shows a list of tunes available for this analysis and recommended frequency. Tuning is done prior to the analytical sequence.

Table 3. MS Tuning Guide

Tune Type	Tune Description	Frequency
EI Diagnostics Only	Runs complete diagnostics and generates report. No tuning is performed.	Used to check and troubleshoot MS
EI Full Tune	Complete EI Tuning. Tunes and sets detector gain to 3 x 10^5.	After cleaning the source, or if EI Tune fails. Follow with EI Tune
EI Tune	Tunes resolution, mass, lenses, adjusts detector sensitivity. Does not tune detector gain.	Every six months, or if Daily Tune Check fails. Follow with Daily Tune Check
Daily Tune Check	Checks mass, performs leak check and generates report with gain from detector sensitivity tune.	Daily

14. Quality Control

Several types of QC samples are analyzed to ensure and assess the quality of the data. These QC samples, acceptance criteria, and corrective actions are described in Table 4. If QC results do not meet criteria, corrective action must be taken.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Extraction Hold Time	All samples	Store samples at or below 5°C until extraction. Extract within 28 days from collection.	Flag, document, and report.
Analytical Hold Time	All sample and QC extracts	Store extracts at or below 5°C until analysis. Analyze within 60 days from extraction.	Flag, document, and report.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Method Blank	One per extraction batch at a minimum	<RL	Check instrument and method materials for possible contamination. Reanalyze the entire extraction batch. If the method blank is still outside criteria, then evaluate sample results. When sample results are less than ten times higher than method blank results, results are invalidated for those samples associated with the method blank.
Solvent Blank	One per analytical batch at a minimum	<RL	Check instrument and method materials for possible contamination (i.e., carryover, solvent contamination). Reanalyze entire analytical batch if needed. If the method blank meets criteria and there are no analytical issues, report results.
Field Blank	Client request or field protocol	<RL	Reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues.
Breakthrough Analysis	One per ten samples at a minimum; also done for high concentration samples (>500 ng/mL)	any chloropicrin detected in the secondary sorbent bed is ≤ RL or ≤ 5% of the concentration in the primary sorbent bed, whichever is greater	Reanalyze breakthrough bed to confirm breakthrough. If reanalysis confirms breakthrough, flag, document, and report.
Initial Calibration	Minimum of five calibration levels prior to sample analyses	$R^2 \geq 0.96$ using a quadratic fit	Reanalyze. Prepare new calibration standards if criteria still not met. Once criteria is met, reanalyze entire analytical batch.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Carryover Check	After analysis of high concentration sample (>500 ng/mL)	<RL	Assess subsequent sample. If chloropicrin is not detected, no further action is needed. If chloropicrin is ≥ the reporting limit, reanalyze the sample to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. If reanalysis results meet replicate criteria, report results. If not, analyze solvent blanks to clean system. Reanalyze subsequent samples once system is clean.
Collocated Samples	Per client request (typically 10% of field samples) or field protocol	Relative Percent Difference (RPD) ± 25% for detections > 5 x RL	Verify results by reviewing data. Report results. Notify client if outside criteria.
Continuing Calibration Verification (CCV)	Mid-point calibration standard. Analyzed after ten or fewer samples and at end of analytical batch	Ending and bracketing CCV must be within 20% of expected value.	Reanalyze CCV that failed and all preceding samples that are not bracketed by CCV that met criteria. Prepare new CCV if criteria still not met. Reanalyze entire analytical batch with new CCV.
Control Standard (CS)	After calibration	CS must fall within established control criteria as described in the QCM	Reanalyze CS. Prepare new CS if criteria still not met. Reanalyze entire analytical batch with new CS.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Replicate	One per ten or fewer samples in analytical batch	RPD ± 25% for detections > 5 x RL	Reanalyze replicate and all associated samples within bracketing standards. If still outside criteria, investigate and correct issues. Reanalyze. Invalidate all samples in analytical batch if replicate fails again.
Laboratory Control Spike (LCS)	One per extraction batch	70-130% of expected value	Reanalyze LCS with the entire analytical batch. If the LCS still does not meet criteria, and all other QC passes, further investigation is required.
Field Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate for possible lab issues if still outside criteria. Report results if no analytical issues are found.
Field Spike Storage	NA	≤5°C when not on the sampler	Flag, document, and report.
Trip Spike Storage	NA	≤5°C	Flag, document, and report.
Trip Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate for possible lab issues if still outside criteria. Report results if no analytical issues are found.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
MDL Verification	Annually and when major maintenance or major changes are done	• Minimum of seven replicates are required • Must meet criteria of MDL < Spike Concentration < 10x MDL • MDL recoveries must be within 50-150% of expected concentrations	Prepare and analyze another set of MDL replicates. If the MDL criteria is still not met, the MDL may be accepted with justification and management approval. This must be documented and placed in the MDL data package.

15. Calculations

15.1. Chloropicrin stock standard concentration is calculated as:

$$\frac{weight\ of\ chloropicrin\ neat\ (mg)}{final\ volume\ (mL)}$$

15.2. Intermediate standard concentrations are calculated as:

$$\frac{stock\ concentration\ \left(\frac{mg}{mL}\right)\ x\ volume\ added\ (mL)\ \ x\ \left(\frac{1000\ \mu g}{mg}\right)\ x\ \left(\frac{1000\ ng}{\mu g}\right)}{final\ volume\ (mL)}$$

15.3. Calibration, control, and LCS standard concentrations are calculated as:

$$\frac{concentration\ of\ intermediate\ standard\ \left(\frac{ng}{mL}\right)\ x\ amount\ spiked\ (\mu L)\ x\ \left(\frac{mL}{1000\ \mu L}\right)}{4\ mL\ extraction\ volume}$$

15.4. Relative Percent Difference (RPD) between two results is calculated as:

$$RPD = \frac{|X1 - X2|}{(X1 + X2)/2}\ x\ 100\%$$

Where:
X1 = first measurement value

$X2$ = second measurement value

15.5. EQL is calculated as:

$$EQL\ in\ ng/sample = 5\ x\ MDL\ \left(\frac{ng}{mL}\right) x\ volume\ extracted\ \left(\frac{mL}{sample}\right)$$

$$EQL\ in\ ng/m^3 = 5\ x\ \frac{MDL\ \left(\frac{ng}{mL}\right)\ x\ volume\ extracted\ \left(\frac{mL}{sample}\right)}{sampling\ volume\ (m^3)}$$

Where:
MDL = MDL value in ng/mL units
volume extracted = 4 mL/sample
sampling volume (flow rate is 0.1 L/min): 24 hrs. = 144 liters = 0.144 m^3

15.6. Field spike recoveries are calculated as:

$$\left(\frac{(field\ spike\ recovered\ amount - collocated\ sample\ recovered\ amount)}{spiked\ amount}\right)\ x\ 100\%$$

15.7. LCS recoveries are calculated as:

$$\left(\frac{LCS\ recovered\ amount}{spiked\ amount}\right)\ x\ 100\%$$

15.8. Trip spike recoveries are calculated as:

$$\left(\frac{trip\ spike\ recovered\ amount}{spiked\ amount}\right)\ x\ 100\%$$

15.9. The concentrations of analyzed samples are initially reported in ng/mL. Ambient air concentrations are reported as ng/sample and are calculated as:

$$raw\ concentration\ \left(\frac{ng}{mL}\right)\ x\ \frac{4\ mL}{sample} = \frac{ng}{sample}$$

16. Data Management and Reporting

Data management consists of samples logged into LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. All anomalies, corrective actions, and management

approved SOP deviations must be documented in the chemist's logbook, monthly QC report, and final data report. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation.

16.1. After data acquisition, the raw data files are processed by the analytical software to produce result files. The result files contain quantitation information such as peak areas and retention times, along with concentration and instrumentation information.

16.2. Peaks found in the chromatogram are verified by retention time and ion spectra to be identified correctly by the chemist. Integration of each peak is evaluated to ensure the software processed the data appropriately. Any improper integration will be amended and documented.

16.3. The instrument method is calibrated for both retention time and concentration during data processing using the integrated calibration standard areas. The concentrations of target compounds are based on the peak areas and the known analyte concentrations in the standards. Concentrations are calculated using the instrument standardization routine for samples, blanks, controls, and spikes. Retention times are checked to ensure no excessive peak shifting (beyond 0.3 minutes) has occurred. If shifting occurs, maintenance may need to be performed. Samples showing excessive retention time shifting will be reanalyzed.

16.4. The final results will be adjusted by an appropriate dilution factor (only if the sample was diluted; otherwise, the dilution factor would be 1.00) and reported in ng/sample.

16.5. All QC and sample results are verified by the chemist and then sent to the LIMS for archive and reporting. Data is reviewed by a peer chemist and approved by management before being released to the client.

16.6. Analyte concentrations will not be reported if below the RL unless otherwise requested by the client. (i.e., DPR may request 5x MDL be reported as "EQL" and concentrations between the MDL and EQL be reported as "Trace".) Instrument performance must be evaluated to ensure there is no matrix interference which could bias any reporting below the RL.

17. Maintenance and Repairs

Preventive maintenance is done on an annual basis on the GC/MS and repairs are done as needed by an approved vendor under contract to MLD or by experienced staff. All maintenance and repairs are documented in a logbook.

18. References

18.1. CARB NLB Laboratory Quality Control Manual Revision 5.0, December 7, 2021

18.2. CARB, “Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street,” November 2021 or current.

18.3. SAS Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Spectrometry Revision 4, 12/01/2010

18.4. California Department of Food and Agriculture, Method EM 16 “Determination of Chloropicrin Desorbed from XAD-4 Resin Tubes” 10/14/1999

19. Revision History

SOP/Addendum Identification	Approval Date	Description of Change
MLD075 Revision 0.0, Analysis of Trichloronitromethane (Chloropicrin) in Ambient Air Using Gas Chromatography/Mass Spectrometry	September 28, 2017	SAS Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Spectrometry Revision 4. 12/01/2010
MLD075 Revision 1.0	January 9, 2023	Revised calibration standard preparation, sample hold time, extraction solvent, and instrument parameters.