Standard Operating Procedure for Analysis of Volatile Pesticide Compounds in Ambient Air Using Gas Chromatograph/Mass Spectrometer

MLD080
Revision 0.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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1. SCOPE

This method describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze volatile pesticides in ambient air samples using a gas chromatograph/mass spectrometer (GC-MS). The method is based on Environmental Protection Agency (EPA) method TO-17. The following list of compounds have been validated for this method.

Compounds	Reporting Limit (RL), ng / sample	Chemical Abstract Service (CAS) Number
cis-1,3-Dichloropropene	8.88	10061-01-5
trans-1,3-Dichloropropene	8.88	10061-02-6
Methyl Isothiocyanate (MITC)	1.00	556-61-6

This standard operating procedure (SOP) was developed by staff in the Organic Laboratory Section (OLS) of the Northern Laboratory Branch (NLB).

2. SUMMARY OF METHOD

Air samples are collected on stainless steel sorbent packed thermal desorption (TD) tubes at sites potentially impacted by nearby pesticide application. The samples are stored at or below five degrees Celsius (°C) from collection until analysis. For analysis the tubes are capped, with specific autosampler caps, and placed into the thermal desorption system. The compounds are released by heating the tube in a back-flush flow of inert carrier gas followed by secondary trapping on the electrically cooled focusing trap within the system. The trapped compounds are then released by heating and back-flushing the sorbent trap onto the gas chromatography column where they are separated and subsequently identified and quantified by the mass spectrometer in the selected ion monitoring (SIM) mode.

3. ACRONYMS

Table 1. Acronyms used in this SOP

Acronym or Term	Definition
ºC	degrees Celsius
AMU	Atomic Mass Units
CAS	Chemical Abstract Service
CCV	Continuing Calibration Verification
CS	Control Standard
CS_2	Carbon Disulfide
EA	Ethyl acetate
GC-MS	Gas Chromatograph-Mass Spectrometer
ICAL	Initial calibration
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation
M/Z	mass-to-charge ratio
MDL	Method Detection Limit
µL	Microliter
MITC	Methyl Isothiocyanate
MLD	Monitoring and Laboratory Division
MSD	Mass Spectral Detector
NLB	Northern Laboratory Branch
NOAA	National Oceanic and Atmospheric Administration
OLS	Organics Laboratory Section
PFTBA	Perfluorotributylamine
PPB	Parts per Billion by Mass
PPBV	Parts per Billion by Volume
PTFE	Polytetrafluoroethylene
QC	Quality Control
QCM	Quality Control Manual
RH	Relative Humidity
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SDS	Safety Data Sheet
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
TD	Thermal Desorption
UHP	Ultra High Purity

4. DEFINITIONS

4.1. ANALYTICAL BATCH – A set of samples analyzed together as a group in an uninterrupted sequence.

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

4.3. CALIBRATION STANDARD – A standard containing the target analytes at a known concentration obtained from a source other than that of the control standard (second source) or from a different lot number.

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

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

4.6. CONTINUING CALIBRATION VERIFICATION (CCV) – A mid-level standard containing the target analytes at a known concentration analyzed once per every ten samples and at the end of every sequence after sample analysis to confirm stability of the instrument.

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

4.8. CONTROL STANDARD (CS) – A standard containing the target analytes at a known concentration obtained from a source other than that of the calibration standard (primary source) or from a different lot number. If a second source is not available, the standard may be prepared by a different person or on a different day. This control contains all target compounds and is used to maintain QC charts.

4.9. DILUTION – Is the process of reducing the concentration of a solute in solution. 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.

4.10. DUPLICATE – A re-analysis of a sample within an analytical batch that is processed through the entire analytical method to show precision.

4.11. HOLD TIME – The maximum amount of time a sample may be stored prior to performing an operation. Analytical hold time for tube analysis is from sample collection to analysis.

4.12. INTERFERENCE – Discrete artifacts or elevated baselines from environmental factors that may cause systematic errors in measurement of the sample being analyzed or misinterpretation of the chromatographic data.

4.13. LIMIT OF QUANTITATION (LOQ) – The minimum concentration or amount of an analyte that a method can measure with a specified degree of confidence. The LOQ is equal to five times the standard deviation of the replicate analysis from the method detection limit (MDL) determination/verification. LOQ is analyte and instrument specific.

4.14. 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% 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 analytes of interest.

4.15. REPORTING LIMIT (RL) – A number which data is not typically reported below. The RL may or may not be statistically determined and may be established by regulatory requirements or in conjunction with client or program needs. The RL is equivalent to or greater than the LOQ.

4.16. SPIKE – A quality control sample employed to evaluate the accuracy of a measurement. A spike is prepared by adding a known amount of the target analyte(s) to an aliquot of the sample or to media prior to sampling. The recovery of a spike provides an indication of the efficiency of the analytical procedure for a given matrix. Spikes can be designated as field, laboratory, matrix, and trip spikes. Field spikes are used to assess matrix interferences.

4.17. STANDARD – (calibration or control standard) – A substance or material with properties believed to be traceable with sufficient accuracy to permit its use to evaluate the same property of another. It is a solution or substance commonly prepared by the analyst to establish a calibration curve or the analytical response function of an instrument.

4.18. SYSTEM / METHOD BLANK – A cleaned sorbent tube used to monitor the laboratory analytical systems for interferences and contamination. These two QC types of blanks are prepared in the same manner (see Section 14), but are independent from one another.

4.19. FIELD BLANK – A 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. Field blanks are typically only done by client request.

4.20. TRIP BLANK – An unopened 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. Trip blanks are typically only done by client request.

5. INTERFERENCES AND LIMITATIONS

5.1. Note that during optimization and validation of this method certain conditions were found to impact recovery of the target compounds. These conditions were:

- Sampling at temperatures above 35 °C.
    - Temperatures exceeding 35 °C are not expected in California during the November to February 'winter' pesticide spraying season.
    - If sampling exceeds this temperature limit then sample results will be flagged.
    - If sampling is expected to regularly exceed these temperatures then the sampling flow and/or duration should be reduced and recovery validated and documented prior to deployment.
- Sampling at an absolute humidity above 17 g/m^3.
    - Online moisture calculators such as those from the National Oceanic and Atmospheric Administration (NOAA) can be used to determine the absolute humidity based off the temperature and relative humidity.
    - The below Table 2 shows a range of conditions that give an absolute humidity of 17 g/m^3.

Table 2. Conditions that give 17 g/m3 absolute humidity

Temperature (°C)	Relative Humidity (%RH)
20	100
25	74
30	57
35	43

    - Checking the conditions for the samples is recommended before analysis to identify potentially impacted samples.
    - If sampling has exceeded this humidity limit then sample results will be flagged.
    - If the sampling conditions are expected to regularly exceed 17 g/m^3 then the method should be adjusted and recovery validated and documented prior to deployment.

5.2. All target compounds are identified by their mass spectrum and retention times. Compounds having similar GC retention times may co-elute or have ion fragments at the same mass-to-charge (m/z) ratio as the target compound. This can lead to misidentification or inaccurate quantitation.

5.3. The analytical system may become contaminated when samples containing high compound concentrations are analyzed. If there is suspected carryover from a high concentration sample, additional system blanks should be analyzed and verified to have results below the RL prior to reanalyzing the succeeding sample(s).

5.4. High boiling point compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column must be baked out to remove these contaminants prior to analyzing samples if present. For example, run the column to usual top temperature and hold for at least 1 hour. 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/or this SOP. Personnel must also be trained 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 must 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 the NLB Chemical Hygiene Plan.

MITC is a breakdown product of metam sodium, metam potassium, and dazomet, which are non-selective soil fumigants used in agriculture. Acute inhalation could cause eye irritation, respiratory, or systemic effects. MITC is also a dermal sensitizer. The analyst should refer to the safety data sheets (SDS) for additional information regarding chemical properties and precautions.

7.1. The analyst must wear protective eyewear, lab coat, and nitrile gloves whenever working with liquid standards, solvents, and solutions. Solvents are flammable; standards are irritants, particularly to the eyes and skin, and possibly very toxic. Refer to the SDS for specifics regarding handling, as well as emergency procedures.

7.2. This method uses high-pressure gases. Follow safe handling practices (as per CARB Health and Safety training or equivalent) regarding compressed gases when moving and installing the cylinders. Use suitable equipment and protective devices, such as carts and safety shoes.

7.3. The TD, GC, and MS have heated zones (refer to applicable instrument manual(s) for specifics), which may cause burns. The cold trap is both heated and cooled. Avoid contact with these zones and devices when in operation and make certain they are de-energized or at ambient temperature prior to servicing by checking temperature gauges.

8. HAZARDOUS WASTE

MITC is classified as a strong lachrymator. All accumulated liquid waste must be stored in an approved waste container. Liquid waste is any form of liquid that is considered hazardous to humans, animals, fish, or the environment. The NLB Health & Safety Coordinator must be notified upon accumulation of 1.0 kg (approximately two pounds) of this waste. Waste consists of liquid MITC and unanalyzed resin tubes used to capture MITC. MITC waste must be stored in waste containers provided for this purpose. The containers must be properly labeled with appropriate hazardous waste labels indicating the contents and start date of accumulation.

Other hazardous waste associated with this analysis consists of used pump oil and solvents. Pump oil is exchanged when serviced, typically on an annual basis. The used oil is collected in a plastic container and stored in the chemical waste unit. Solvents for disposal are stored in suitable waste containers and should be properly labeled with the accumulation start date. Satellite accumulation containers must be disposed of within 1 year of the accumulation start date. The NLB Health & Safety Coordinator must be notified before the 1 year from the accumulation start date, or when the container is full and needs to be disposed, whichever comes first. Once the satellite container is full, it may be moved to the central hazardous waste storage area. It is stored there until removed by the contracted hazardous waste company for disposal.

9. EQUIPMENT AND SUPPLIES

9.1. Gas chromatograph with a programmable oven, electronic pressure control for capillary columns and heated injector.

9.2. Column: Restek Rtx-200, 60 meter, 320 µm inner diameter, 0.5 µm film thickness, or equivalent.

9.3. Detector: mass spectral detector (MSD).

9.4. Software: A data station for control of GC, MS plus storage and quantification of mass spectral data (see References Section 22 for details).

9.5. Refrigerator which can maintain a minimum low temperature of 4 °C.

9.6. Adsorbent cold trap, such as a Markes part no. U-T9TNX-2S cold trap, or equivalent.

9.7. Stainless steel sorbent tubes packed with a suitable sorbent(s) for the target compounds, such as Markes ‘universal’ tubes (part no. C3-AAXX-5266), or equivalent.

9.8. Brass storage caps for the sorbent tubes, ¼ inches Swagelok type brass fittings with Polytetrafluoroethylene (PTFE) ferrules.

9.9. Sample concentrator and sorbent tube auto-sampler, such as a Markes TD-100-xr, or equivalent.

9.10. Hamilton microliter (µL) syringes (or equivalent): 10 µL, 25 µL, 250 µL, and 1000 µL volume ranges.

9.11. Hamilton gas-tight syringes (or equivalent) with suitable needle tips: 50 mL and 500 mL.

9.12. Sorbent tube calibration standard loading rig, such as from Markes or equivalent.

9.13. Sorbent tube conditioner, such as Markes TC-20, or equivalent.

9.14. 4 mL glass storage vials with Teflon lined screw caps, such as VWR (part# 66009-876).

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

9.16. Volumetric Flasks: 5 mL, 10 mL, 25 mL, 50 mL, and 100 mL volume ranges.

9.17. Analytical balance capable of weighing as low as 0.1mg, with calibrated weight kit.

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

9.19. Disposable Pasteur pipettes, 1.5 mL such as Baxter Scientific Products (part# P5200-2).

9.20. Tweezers.

9.21. Disposable nitrile or neoprene gloves to handle organic solvents.

10. REAGENTS AND GASES

Consult the latest version of NLB's Laboratory Quality Control Manual (QCM) for the calibration gas requirements.

10.1. Carbon disulfide 99.9+ percent, less than 100 parts ppb benzene such as EMD OmniSolv item # CX0396-6.

10.2. Ethyl acetate, pesticide grade or better such as EMD OmniSolv item # EX0242-1 or equivalent.

10.3. MITC, neat standard such as Chem Service (item # MET-12392A-1G) or equivalent. Two different lot numbers or sources if possible (for calibration and control standards).

10.4. Gas standards containing cis- and trans-1,3-dichloropropene, such as EPA TO-14/15 from Restek or AirGas at 100 ppbV. Two different lot numbers or sources if possible (for calibration and control standards).

10.5. Perfluorotributylamine (PFTBA) or MS tune solution.

10.6. Ultra High Purity (UHP) Helium, 99.999% for use as the GC column carrier gas.

10.7. UHP Nitrogen, 99.999% for use on the calibration standard loading rig and sorbent tube conditioner.

11. STANDARDS PREPARATION

All standard solutions are stored refrigerated at < 5 °C until used. The standard solutions are removed from the freezer and allowed to equilibrate to room temperature before use. Neat standards are valid up to the manufacturer's expiration date. Working standards expire one year from preparation date but not to exceed the expiration date of the neat standard.

For gas cylinders, the Certificate of Analysis shall reflect the actual analysis of the specific cylinder, as evidenced by cylinder number. The analytical uncertainty of each compound must be less than ±10% of the actual concentration.

Standards should not be used past the expiration date issued by the vendor unless stability can be verified against a non-expired standard. If used past the expiration, management approval and documentation comparing concentration to historical data is required.

11.1. Percent Carbon Disulfide (CS_2) in Ethyl Acetate (EA)

To prepare the 0.1 percent CS_2 in EA solution, partially fill a 500 mL volumetric flask with EA. Add 500 µL CS_2 to the flask. Fill the flask to volume with EA and invert several times to mix. This solution is used for all MITC standard, QC, and sample preparations.

11.2. Calibration Standards

A 1,000 µg/mL MITC stock standard is prepared by weighing out approximately 0.025 grams neat MITC in a 25.0 mL volumetric flask and filling to volume with 0.1 percent CS_2 in EA. Three intermediate standards are made using the preparation scheme in Table 3, with 0.1 percent CS_2 in EA as the diluent. Depending on the actual weight of neat MITC weighed out, the final concentrations may be adjusted accordingly.

Table 3. MITC Stock and Intermediate Standards Preparation

Standards	Amount	Vol Flask Size (mL)	Final Concentration (µg/mL)
Stock	0.025 g	25.0	1,000
Intermediate A	0.25 mL of Stock	5.0	50
Intermediate B	0.5 mL of A	5.0	5
Intermediate C	0.5 mL of B	5.0	0.5

For example, Intermediate B at 5 µg/mL is made using a 0.5 mL aliquot of the 50 µg/mL MITC Intermediate A in a 5 mL volumetric flask and filling to volume with 0.1 percent CS_2 in EA.

11.3. Control Standard (CS)

11.3.1. A CS stock standard is prepared in the same manner as described in Section 11.2, using a second source standard when possible. A 10 µg/mL CS intermediate is prepared by diluting a 10 µL aliquot of the CS stock to 1 mL, using 0.1 percent CS_2 in EA as the diluent. The CS standards may be prepared by a second analyst if a second source standard is not available.

11.3.2. A CS is analyzed after the calibration curve. The CS criteria are based on control limits, which are established as described in the NLB Quality Control Manual.

11.4. Injecting standards to sorbent tubes

Calibration standards: Table 4 lists suggested calibration curve levels, which can be adjusted as needed depending on expected sample concentrations. Both liquid and gas standards are injected to each sorbent tube.

Table 4. Calibration Levels

Calibration Level	MITC Standard	Spike Volume for MITC standard (µL)	TO-15 Gas Standard (nominal 100 ppbV) Volume (mL)
1	C (0.5 µg/mL)	1.0	5
2	C (0.5 µg/mL)	2.0	10
3	B (5 µg/mL)	1.0	20
4	A (50 µg/mL)	0.5	200
5	A (50 µg/mL)	1	500

11.4.1. Liquid standards are injected before gaseous standards.

11.4.2. Liquid standards are introduced to the sorbent tube using a suitably sized (e.g., 10 µL) liquid syringe and the calibration standard loading rig.

11.4.3. Gaseous standards are introduced to the sorbent tube using a suitably sized gas tight syringe and the calibration standard loading rig.

11.4.4. Steps to use the calibration standard loading rig are as follows:

11.4.4.1. Insert tube with grooved (sampling) end of the tube into the loading rig and hand tighten in place.

11.4.4.2. Toggle on gas flow and using a flow meter set to approximately 150 mL/min.

11.4.4.3. Fill syringe with desired volume of liquid/gas standard.

11.4.4.4. Insert needle of the syringe through septum on the loading rig slowly until the front gauze of the tube is reached (which is felt through increased resistance).

11.4.4.5. Retract the needle 1-2 mm and inject.

11.4.4.6. Repeat previous 2 steps for additional gas/liquid standards.

11.4.4.7. Leave tube attached and gas flowing for 2 minutes.

11.4.4.8. Remove and cap tube.

11.4.4.9. Turn off gas flow to the loading rig once finished.

12. FIELD SPIKES AND TRIP SPIKES

These spikes are prepared in the laboratory at client request only. Field spikes are sampled and analyzed with the un-spiked collocated sample. With the spiked and un-spiked sample, a percent recovery can be determined. The data obtained from these spikes can serve as an indication of matrix interferences.

12.1. All tubes used must be conditioned prior to use (see Section 14 for instructions).

12.2. Follow the standard loading procedure from Section 11 to prepare the appropriate number of field spikes and trip spikes, as required by the sampling protocol.

12.3. The tubes are capped and labelled with the date, time, and description (either “field spike” or “trip spike”).

12.4. Store the tubes below 5°C.

12.5. The spiked and un-spiked tubes are analyzed on a GC-MS in the same manner as any other sample.

12.6. Spike samples are required to have the percentage recovery evaluated and the criteria can be found in Section 17, Table 5 of this SOP.

13. SAMPLE STORAGE AND HOLD TIME

13.1. Upon receipt of samples verify the temperature has been maintained below 5 °C, if not the sample is flagged in LIMS and analyzed.

13.2. Check the brass storage caps are securely fitted, if not then the sample is flagged in LIMS and analyzed.

13.3. The samples are stored refrigerated at < 5 °C until analysis.

13.4. Samples are analyzed within 30 days of sample collection.

14. BLANK PREPARATION

14.1. A method or system blank is accomplished by running a clean tube.

14.2. The TC-20 tube conditioner is used to clean/condition the sorbent tubes. The TC-20 can clean/condition up to 20 tubes at a time.

14.3. Conditioning at 300 °C for at least 90 minutes with a flow of 50 mL/min nitrogen.

14.4. For tubes due to be sent out as sampling media, including field blanks and trip blanks, a minimum of two tubes per cleaning batch is analyzed and verified to be < RL.

14.5. If tubes fail to meet the < RL requirement, they should be conditioned again. If samples are routinely at high levels then implementing a longer conditioning time is recommended.

14.6. The method/system blanks must meet the criteria summarized in Table 5 for samples to be analyzed and reported.

15. SAMPLE PREPARATION

15.1. Samples must be equilibrated to laboratory room temperature, with their storage caps still fitted, prior to analysis.

15.2. Remove the brass storage caps.

15.3. Fit the autosampler caps and place into the autosampler trays, noting the grooved end of the tube should be on the right side of the tray.

15.4. Create a sample/sequence list on the workstation computer for the samples to be analyzed.

15.5. Enable sample re-collection in the Markes TD sequence for entire analytical batch to allow for as needed future re-analyses.

16. ANALYSIS

16.1. Instrument Performance Check

16.1.1. The MS must be tuned with calibration gas PFTBA to meet the tuning and standard abundance criteria prior to initiating any data collection. The detector is tuned using the Autotune program. The procedure and the criteria for the PFTBA tune can be found in the GC system manuals.

16.1.2. The tune value, with regards to positions and abundance ratios of the tune m/z and their corresponding isotope m/z's, must be reviewed. Refer to applicable manual for specific criteria.

16.1.3. The system must be checked for leaks and the electron multiplier voltage must be checked and evaluated. Corrective action must be performed if needed prior to analyzing samples. Refer to applicable manual for specific criteria.

16.1.4. The tuning report must be saved and archived with associated sample data.

16.1.5. Verify beginning QC meets criteria in Table 5 prior to analyzing samples.

16.2. Sample Concentration and Analysis

16.2.1. Samples are introduced onto the sorbent trap under control of the thermal desorption equipment and method. These parameters are described in the Appendix OLS-MLD080-A1.

16.2.2. After the sorbent trap has finished loading, it is dry purged with helium gas, heated, and the contents are transferred to the GC. The instrument conditions used are described in Appendix OLS-MLD080-A2.

16.2.3. The ambient samples are analyzed using the same methods as used for the calibration and control standards.

16.3. Analytical Sequence

16.3.1. Each analytical run of 10 or fewer samples must include a PFTBA tune, initial calibration (ICAL), control standard, system and method blanks, duplicates and CCV.

16.3.2. Below is the required order of analysis for a valid batch:

- PFTBA Tune
- System Blank
- Initial Calibration (ICAL)
- Control Standard
- Method Blank
- Samples (up to 10)
- Duplicate (one every 10 or fewer samples)
- Method Blank
- CCV (analyzed once per every ten samples and at the end of every sequence)

16.4. Instrument Method

A typical method is shown in the Appendix, OLS-MLD080-A1 and OLS-MLD080-A2.

17. QUALITY CONTROL

All QC, samples, duplicates, and additional injections must be analyzed within a 24-hour time period from the injection time of the valid ICAL for the batch to be considered valid and reportable.

Several types of QC samples are evaluated daily, annually, or as needed to verify the instrument is still under control and meet the required acceptance criteria. These are described in Table 5 below. If QC results are not met, corrective action(s) must be taken. Occasionally, deviations may be necessary which shall require documentation and management approval prior to use. These deviations must be documented on the data review checklist in the daily batch packet and final data packages.

Table 5: Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
PFTBA Tune	Analyze before the initial calibration.	Autotune done by instrument marks as passed and/or meets manufacturer's criteria.	• Check Air/Water, background and level of tune standard. • Adjust parameters to improve sensitivity. • Run a full tune followed by an Autotune. • Clean source. • Contact manufacturer if tuning continues to fail. No samples are analyzed.
Initial Calibration	Minimum of five calibration levels prior to sample analyses.	$R^2 \geq 0.98$. Using a linear or quadratic fit.	• A linear or quadratic fit can be used, whichever gives the best accuracy across the points of the curve. • If the calibration curve fails, re-analyze. Prepare new calibration standards if criteria not met. • If calibration continues to fail, stop, and begin corrective actions to determine the cause of repeated failures (specifics include instrument maintenance and tube issues).
CCV	Analyzed after 10 or fewer samples and at end of the sequence.	Calculated concentration within ± 25% of expected and ± 0.300 minutes of the CCV level of the Initial Calibration.	• 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 all samples with new CCV.
Control Standard	Analyzed once after the initial calibration.	Must fall within established control criteria as described in the QCM.	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another control standard or prepare new control standard and re-analyze. • If the control standard fails for select compound(s) and the sample cannot be reanalyzed, those compounds are invalidated with NLB management approval. Document exceedances. • Re-establish Control Limits.
System Blank	Analyzed before initial calibration.	<RL.	• If initial system blank is equal to or above RL, additional system blanks can be analyzed to clear the analytical system of possible contamination. • The cause of contamination is investigated; and resolved before the rest of the sequence is run.
Method Blank	Run after the control standard and before the CCV.	<RL.	• If the method blank result is equal to or higher than the RL, the following apply: • If sample results are at least 10x higher than the blank result, it is documented on the daily QC package, but no additional corrective action is required. • If sample results are less than 10x higher than the blank result, the analysis results for those samples are invalid. • The cause of contamination is investigated; the entire batch is re-analyzed if required and if sample is available.

QC Type	Frequency	Criteria	Corrective Action
Field Blank / Trip Blank	Client request or field protocol.	<RL.	• If ≥ RL reanalyze to confirm results. Investigate if still outside criteria. Flag and report results if no analytical issues.
Contamination Check	For tubes due to be sent out as sampling media, including field blanks and trip blanks, a minimum of two tubes per cleaning batch is analyzed.	< RL.	• If ≥ RL repeat tube cleaning/conditioning and repeat the contamination check. • If still ≥ RL replace the tube(s).
Sample Hold Time	All samples.	Store tubes < 5°C until analysis. Analyze within 30 days from collection.	• If hold time or temperature is exceeded, samples are flagged, documented, and reported.
Sampling Conditions Check	All samples.	Maximum temperature ≤ 35°C and absolute humidity ≤ 17 g/m^3.	• If local meteorological data indicates > 35°C during sampling document, and flag and report results. • If absolute humidity > 17 g/m^3 (calculated using average temperature and humidity during sampling and an on-line calculator such as that from NOAA), document, and flag and report results.
Brass Cap Integrity Check	All samples.	Checks caps aren't loose or have fallen off.	• If caps are loose or have fallen off, samples are flagged, documented, and reported
Duplicate	1 per 10 or fewer samples in analytical batch.	RPD ± 25%.	• If RPD exceeds ± 25%, evaluate. • If primary and duplicate samples have results <5x RL, no need to notify management. Report results. • If both sample results are ≥5x RL and the RPD > 25%, re-analyze duplicate and all associated samples in the batch. If still outside criteria, investigate and correct issues, re-analyze. Invalidate all samples in batch if duplicate fails again.
Collocated Samples	10% of field samples or per field protocol.	RPD ± 25%.	• If RPD exceeds ± 25%, evaluate. • If primary and collocated samples have results <5x RL, no need to notify management. Report results. • If both primary and collocated results are ≥5x RL, notify NLB management, report results and document.

QC Type	Frequency	Criteria	Corrective Action
Carryover Check	After analysis of high concentration sample exceeding upper linear range.	No target analytes detected above RL.	• Analyze one or more system blanks to clean system. • Evaluate subsequent sample(s) if < RL then no further action is necessary, otherwise re-run to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. Duplicate criteria is used to confirm results. • Re-analyze high-level sample at a dilution to get target analyte within the linear calibration range. • Report first analysis for all compounds within the calibration range and report the dilution analysis for the compounds that exceeded the calibration range in the initial analysis.
Field Spike	Per client request or field protocol.	70-130% of expected value.	• Re-analyze to confirm results. • Investigate if still outside criteria. • Report results if no analytical issues and control standard meets criteria. • Results outside criteria are flagged.
Trip Spike	Per client request or field protocol.	70-130% of expected value.	• Re-analyze to confirm results. • Investigate if still outside criteria. • Report results if no analytical issues and control standard meets criteria. • Results outside criteria are flagged.
MDL Verification	To be verified annually, and when major maintenance or major changes are done.	• Minimum of seven replicates are required. • Must meet window criteria of MDL < Spike Concentration < 10x MDL. • MDL recoveries, against expected concentrations, must be within 50-150%.	• If the MDL criteria is not met, 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.

18. CALCULATIONS

18.1. 0.1 percent CS_2 in EA is calculated as:

$$\frac{amount\ CS_2\ spiked\ (\mu L)\ x\ \left(\frac{mL}{1000\ \mu L}\right)}{final\ volume\ (mL)}\ x\ 100\%$$

18.2. MITC stock standard concentration is calculated as:

$$\frac{weight\ of\ MITC\ neat\ (g)\ x\ \left(\frac{1000\ mg}{g}\right)\ x\ \left(\frac{1000\ \mu g}{mg}\right)}{final\ volume\ (mL)}$$

18.3. Intermediate standard concentrations are calculated as:

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

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

$$\%RPD = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}\ x\ 100$$

X_1 = First measurement value
X_2 = Second measurement value

18.5. Relative Standard Deviation (RSD) for Control Limits is calculated as:

$$RSD = \frac{S}{\overline{X}}\ x\ 100$$

S = Standard Deviation
$\overline{X}$ = Sample Mean

18.6. Field spike recoveries are calculated as:

$$\left(\frac{Field\ spike\ sample\ concentration - Collocated\ sample\ concentration}{Spiked\ Amount}\right) x\ 100\%$$

19. DATA MANAGEMENT AND REPORTING

19.1. 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, archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are always to be kept with the instrumentation.

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

19.3. All target compounds must be confirmed with spectral information from a standard or MS library. Chromatographic peak integrations performed by the analytical software should be reviewed by the analyst. Any re-integrations (manual changes to the baseline) amended by the chemist are documented in the processing software.

19.3.1. Retention times are visually evaluated to confirm that the peaks are not shifting more than ± 0.300 minutes compared to the CCV level of the ICAL. If shifting occurs, re-analyze the samples with the RT shifting.

19.4. Data Transfer to LIMS

19.4.1. Data from the analytical instrument are transferred into LIMS via a data transfer software (i.e., LIMSLink). Data transfer software is also programmed to check results against QC criteria in LIMS before data transfer. Post data transfer, the analyst will review the raw data and QC data transfer and apply corrective action(s) as needed.

19.5. Reporting Results

19.5.1. All data will be reviewed by the analyst, peer reviewed, and approved by management as per the NLB QCM before being released to the client.

19.5.2. 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.

19.5.3. Analyte concentrations will not be reported below the RL unless otherwise requested by the client and approved by NLB management.

20. MAINTENANCE AND REPAIRS

Preventative maintenance is done on an annual basis on the autosampler, concentrator, and GC-MS. Repairs are done as needed by an approved vendor under contract to MLD or by a staff member experienced in the repair. Any preventive maintenance and/or repairs completed are documented in a logbook stored near the instrument or recorded in the instrument log files.

21. REFERENCES

21.1. EPA TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes https://www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf

21.2. CARB NLB Laboratory Quality Control Manual Revision 5.0, December 7, 2021 or current.

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

21.4. Trace 1300 and Trace 1310, Gas Chromatographs, Hardware Manual, Thermo Fisher Scientific, January 2016. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-31715002-GC-TRACE-1300-1310-Hardware-Man31715002-EN.pdf

21.5. Trace 1300 and Trace 1310, Gas Chromatographs, User Guide, Thermo Fisher Scientific, January 2016. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-31715003-GC-TRACE-1300-1310-User-Man31715003-EN.pdf

22. APPENDICES

Appendix 1 (OLS-MLD080-A1): Typical Thermal Desorption Methods for MLD0780.
Appendix 2 (OLS-MLD080-A2): Typical GC-MS Methods for MLD080.

23. Revision History

SOP/Addendum Identification	Approval Date	Description of Change
MLD080 Revision 0.0	January 20, 2023	New method for the analysis of Volatile pesticides in ambient air using Gas Chromatography/Mass Spectrometry

Appendix 1

OLS-MLD080-A1

Typical Thermal Desorption Methods for MLD080

Note – These operating conditions are specific to CARB's use of Markes units with a Thermo GC-MS. Method parameters may change if needed by an experienced analyst and by management approval.

Markes units with a Thermo GC-MS

Standby – Split On; 10 mL/min
Flow Path – 120 °C
GC Cycle Time – 15 minutes
Minimum Carrier Pressure – 5 psi

Dry purge: 2 min at 50 mL/min
Tube desorb time: 10 mins at 300 °C, trap in line at 10 mL/min, split on at 70 mL/min
Trap Purge – 2 minutes at 50 mL/min
Trap Low – 5 °C
Trap High – 250 °C
Trap Heating Rate – 20 °C/s
Trap Hold – 1 minutes; split on at 30 mL/min

Appendix 2

OLS-MLD080-A2

Typical GC-MS Methods for MLD080

Note – these operating conditions are specific to CARB's use of a Thermo GC-MS. Method parameters may change if needed by an experienced analyst and by management approval.

Thermo GC Parameters:
Front Inlet – Off
Front Inlet Flow Mode – FlowCtrl
Front Inlet Pressure Control – Off
Front Inlet Flow Control – On
PrepRun Timeout – 999.99 minutes
Equilibration Time – 0.100 minutes
Ready Delay – 0.100 minutes
Front Inlet Split Mode – Splitless
Front Inlet Split Flow – Off
Front Inlet Flow – 2.400 mL/min

Thermo Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)
0.00	60	1.00
15.00	130	0.00
35.00	250	3.00

Thermo MS Parameters:
Ion Source (Thermo MS) – 310 °C
MS Transfer Line – 230 °C
Ionization Mode – EI

Time (minutes)	Range (amu)	Dwell/Scan Time (seconds)	Detector Gain
4.10	45-300	0.2	$3.00x10^5$
4.10	72, 73, 75, 110, 112, 117, 119, 121	0.006	$3.00x10^5$
9.00	45-300	0.15	$3.00x10^5$