Standard Operating Procedure for the Analysis of Methyl Isothiocyanate (MITC) In Ambient Air Using Gas Chromatography/Mass Spectrometry

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Standard Operating Procedure Analysis of Methyl Isothiocyanate (MITC) in Ambient Air Using Gas Chromatography/Mass Spectrometry

1. Scope

This standard operating procedure describes the determination of methyl isothiocyanate (MITC) in ambient air samples using a gas chromatograph/mass spectrometer (GC/MS). The procedure is for the analysis of MITC collected on coconut based charcoal resin tubes. This SOP is used in conjunction with the NLB Laboratory QC Manual and applicable instrument and software manuals.

2. Summary of Method

Air samples are collected on charcoal resin tubes that are placed on a sampler for 24 hours at a flow rate of 0.5 liters per minute (L/min). The samples are stored at or below four degrees Celsius (°C) until extracted with 5.0 mL of 0.1 percent carbon disulfide (CS_2) in ethyl acetate (EA). The extract is analyzed by a GC/MS in the selected ion monitoring (SIM) mode. Sample analysis and quantitation uses an external standard method for instrument calibration.

3. Acronyms

Acronym or Term	Definition
°C	Degrees Celsius
CARB	California Air Resources Board
CCV	Continuing Calibration Verification
CS	Control Standard
CS_2	Carbon Disulfide
EA	Ethyl Acetate
EI	Electron Ionization
EQL	Estimated Quantitation Limit
GC/MS	Gas Chromatography/Mass Spectrometry
LCS	Laboratory Control Spike
LIMS	Laboratory Information Management System
L/min	Liters Per Minute
LOQ	Limit of Quantitation
MDL	Method Detection Limit

Acronym or Term	Definition
MITC	Methyl Isothiocyanate
MLD	Monitoring and Laboratory Division
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
QC	Quality Control
QCM	Quality Control Manual
RPD	Relative Percent Difference
SDS	Safety Data Sheet
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
UHP	Ultra-High Purity

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, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value.

4.2.1. METHOD BLANK - A charcoal resin tube that is free of analytes and matrix which 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 analytical batch of samples to indicate any contamination or artifacts that may come from the reagents and analytical steps.

4.2.3. FIELD BLANK – A charcoal resin 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 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.

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

4.4. BREAKTHROUGH ANALYSIS – Breakthrough analysis refers to analyzing the secondary sorbent bed of the charcoal resin tube to determine if any amount of sample was not retained in the primary sorbent bed.

4.5. BREAKTHROUGH THRESHOLD LIMIT – The concentration found in the primary sorbent bed that would require analysis of the secondary sorbent bed. The default breakthrough threshold limit for MITC was determined via a breakthrough study to be 10 µg/mL.

4.6. CALIBRATION CURVE – The calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.

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 concurrently with test samples to confirm the stability of the instrument calibration.

4.11. CONTROL STANDARD (CS) – A standard containing an aliquot of the target analyte at a known concentration obtained from a separate source or manufacturer if possible, other than that of the calibration standards.

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 QC (Method Blank, LCS) 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 are 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 NLB's Quality Control Manual.

4.18. REPLICATE – An additional analysis of the same sample or sample extract. The sample extract used for replicate analyses must be chosen at random. Replicate analyses are used to evaluate analytical precision but

not the precision of sampling, preservation, or storage internal to the laboratory.

4.19. 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. Detections below the reporting limit are typically reported as "< RL" unless otherwise requested by the client.

4.20. SPIKES – 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 – A charcoal resin 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) – A charcoal resin 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 – A charcoal resin 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) are evaluated, and if deemed necessary, 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. If ghost peaks are present, the column is baked out to remove these contaminants. 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 LIMS functionality pertaining to the program.

Personnel should provide an initial demonstration of capability to lead staff and/or the section manager 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.

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.

The handling and preparation of samples, extracts, and standards must be conducted in a fume 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. See applicable instrument manual for details.

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 (H&SC) 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.

9. Equipment and Supplies

9.1. Gas Chromatograph: system with instrument controller and software, 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

9.3. GC inlet liner: 4mm x 6.5mm x 78.5mm splitless such as Restek Cat. No. 22406

9.4. Detector: single quadrupole Mass Selective Detector

9.5. Freezer (used to store standards and sample extracts) which can maintain a minimum low temperature of 4 °C.

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

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

9.8. 4 mL glass storage vials with Teflon lined screw caps such as VWR (part# 66009-876)

9.9. Screw-cap test tubes long enough to house the coconut charcoal resin tubes, such as Globe Scientific part # 89497-770

9.10. Ultrasonic bath such as Branson model 8510

9.11. 8 mL glass extraction vials such as Kimble Chase (part# 60940A-8)

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

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

9.14. Volumetric Flasks: 10 mL, 25 mL, and 500 mL volume ranges

9.15. Coconut charcoal resin tubes: 200/400 mg sorbent such as SKC Anasorb CSC coconut charcoal 8 x 110 mm, Cat. No. 226-09

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

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

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

9.19. Tweezers

9.20. Hand-held glass cutter

9.21. Disposable nitrile or neoprene gloves to handle organic solvents

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

10. Reagents

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

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

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

11. Standards Preparation

All standard solutions are stored in a freezer at or below 4°C until used. The standard solutions are removed from the freezer and allowed to equilibrate to room temperature before use. Neat standards should be returned to the freezer at the end of the workday. Working standards in autosampler vials may be stored on the GC autosampler and used repeatedly throughout the work week. Neat standards 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.

11.1. 0.1 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 10,000 µg/mL MITC stock standard is prepared by weighing out approximately 0.25 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 1, 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 1. MITC Stock and Intermediate Standards Preparation

Standards	Amount	Vol Flask Size (mL)	Final Concentration (µg/mL)
Stock	0.25 g	25.0	10,000
Intermediate A	6.25mL of Stock	25.0	2,500
Intermediate B	0.25 mL of Stock	25.0	100
Intermediate C	2.5 mL of B	25.0	10

For example, Intermediate B at 100 µg/mL is made using a 0.25 mL aliquot of the 10,000 µg/mL MITC stock standard in a 25 mL volumetric flask and filling to volume with 0.1 percent CS_2 in EA.

11.2.1. Calibration standards: Table 2 lists suggested calibration curve levels. Six calibration levels ranging from 0.01 µg/mL to 10.0 µg/mL is recommended. These standards are made by spiking aliquots of Intermediate A, B, or C onto the primary sorbent bed of charcoal resin tubes. The tubes are extracted with 0.1 percent CS_2 in EA (total extraction volume of spike plus extraction solvent is 5.0 mL) and sonicated at ambient temperature for one hour (see section 13.1). The extracts are filtered and stored in a freezer at or below 4°C.

Table 2. MITC Calibration Standards Preparation

Calibration Level	Intermediate Standard	Spike Volume (µL)	Extraction Volume (µL)	Final Concentration (µg/mL)
1	C (10 µg/mL)	5.0	4995.0	0.01
2	C (10 µg/mL)	25.0	4975.0	0.05
3	B (100 µg/mL)	5.0	4995.0	0.1
4	B (100 µg/mL)	25.0	4975.0	0.5
5	A (2,500 µg/mL)	10.0	4990.0	5.0
6	A (2,500 µg/mL)	20.0	4980.0	10.0

11.3. Control Standard (CS)

A CS stock standard is prepared in the same manner as described in section 11.2.1, using a second source standard when possible. A 250 µg/mL CS intermediate is prepared by diluting a 0.625 mL aliquot of the CS stock to 25 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.

A 1 µg/mL CS is prepared from the 250 µg/mL intermediate CS standard by spiking a 20 µL aliquot onto a charcoal resin tube, which then goes through the extraction process as described in section 13.1. The CS is stored in a freezer at or below 4°C.

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, Section 12.3.

11.4. Laboratory Control Spike (LCS)

A 0.3 µg/mL LCS is prepared by spiking 15 µL of Intermediate B onto a charcoal resin tube. The spiked resin tube is taken through the extraction process along with its corresponding samples, as described in section 13.1. One LCS is to be extracted and analyzed with every extraction batch.

11.5. Field Spikes and Trip Spikes

11.5.1. Field spikes and trip spikes at 0.3 µg/mL are prepared by adding 15 µL of Intermediate B to a charcoal resin tube. The resin tube must be labeled with the date, time, and description (either “field spike” or “trip spike”). Spiked tubes are placed in individual screw-top test tubes, and stored in a freezer at or below 4°C.

11.5.2. The frequency and number of field spikes and trip spikes collected are determined per project requirements. The client may opt to not utilize field spikes or trip spikes in their project.

12. Sample Storage

12.1. Field Sample Storage - The field operator will place the collected samples/QC in individual screw-top test tubes and store them in a cooler with dry ice at 4°C or less until returned to the laboratory. Temperature indicator strips which indicate below 5°C and above 25°C are packed with the samples. Receipt temperature is documented on the sample chain of custody.

12.2. Laboratory Sample Storage - Upon arrival in the lab, the samples/QC will be stored in a freezer at or below 4°C until extraction.

13. Sample Extraction and Analysis

13.1. Sample Preparation and Extraction

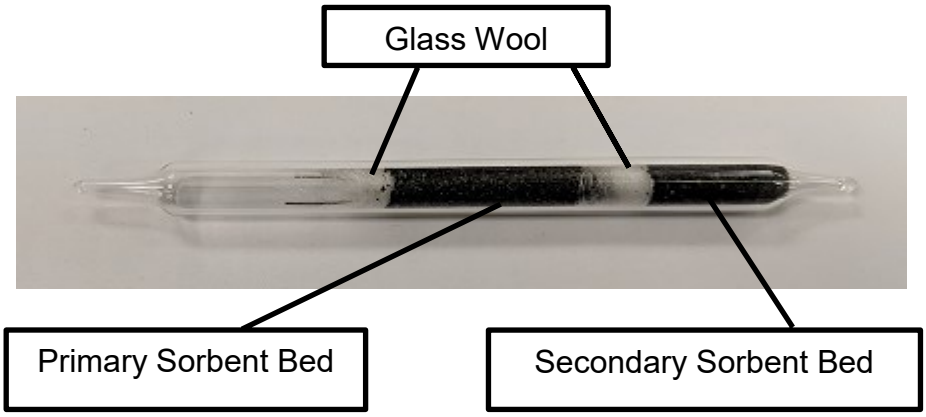
13.1.1. Samples collected on charcoal resin tubes are stored in a freezer at or below 4°C until extraction. Prior to sample analysis, the samples are removed from the freezer and allowed to equilibrate

to room temperature. All samples must be extracted within 28 days of sampling.

13.1.2. Obtain the necessary amount of 8 mL glass vials (one for each charcoal resin 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 charcoal resin tube is comprised of two sections separated by glass wool. The longer end (primary sorbent bed) is used for sample analysis and the short end (secondary sorbent bed) is used for breakthrough analysis. One breakthrough analysis is done for every ten samples, at a minimum.

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



13.1.5. Pour the charcoal resin 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 5.0 mL of 0.1 percent CS_2 in EA, collecting the solvent in the 8 mL glass vial containing the primary resin bed. Cap the vial securely.

13.1.7. If breakthrough analysis is being done, a unique identifying name (indicating that it is a breakthrough sample) and LIMS number is assigned to the breakthrough sample. Extract the secondary sorbent bed as described for the primary sorbent bed in section 13.1.4 – 13.1.6.

13.1.8. If breakthrough analysis is not being done, the secondary chamber is capped off and stored in a freezer at or below 4°C until analysis of the primary chamber is complete. If analysis of the primary chamber does not result in MITC detection over the breakthrough threshold limit, the secondary chamber may be disposed of after the final results are reviewed. If the primary chamber reaches the breakthrough threshold limit, then a breakthrough analysis is performed on the secondary chamber described in section 13.1.7.

13.1.9. Prepare a method blank with every extraction batch by opening an unused, clean charcoal resin tube.

13.1.10. Prepare an LCS with every extraction batch by opening an unused, clean charcoal resin tube and spiking the resin with 15 µL of Intermediate B onto the primary sorbent bed.

13.1.11. Repeat steps 13.1.4 through 13.1.7 for the field spike, trip blank, trip spike, and all samples scheduled for analysis.

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

13.1.13. After sonication, allow the extracts to equilibrate to room temperature. Filter each extract into individual 4 mL glass vials using a 3 mL disposable syringe and a disposable 0.20 µm syringe filter. Label each one clearly with the standard name and extraction date for each sample.

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

13.1.15. 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.

13.1.16. Transfer approximately 250 µL of the calibration standards and control standard into individual 1.5 mL auto sampler vials equipped with a vial insert. The extracts and standards are now ready for analysis. If extracts cannot be analyzed on the day of extraction, place the extracts in a freezer at or below 4°C. Extracts stored in a freezer must be allowed to equilibrate to room temperature prior to analysis.

13.1.17. All extracted samples must be analyzed within 28 days of extraction.

13.2. Sample Analysis

13.2.1. Analytical Sequence

Each analytical run of ten or fewer samples includes the following quality control samples as listed below. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Solvent blank
- LCS
- Method Blank
- Samples (up to ten including potential breakthrough analysis 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. GC/MS Analytical Conditions

GC:

- Injection port temperature: 210°C
- Injection volume: 1.0 µL
- Splitless injection: split flow 50.0 mL/min, splitless time 1.0 min
- Purge flow 5.0 mL/min, constant septum purge
- GC temperature program:
  Oven initial 40°C, hold 1 min
  Ramp to 61°C at 2°C/min, hold for 0.2 min
  Ramp to 240°C at 25°C/min, hold 0.5 min

Run time: 19.36 min

- Retention time: MITC at approximately 11.5 min
- Column flow: helium, constant flow at 1.6mL/min

MS:

- Mass spectrometer: electron ionization
- Transfer line temperature: 245°C
- Ion source temperature: 250°C
- Selective Ion Monitoring: MITC: 73 (quantitation ion), 72 (qualitative ion)

Minor adjustments to GC and MS analytical conditions may be made as needed.

Instrument tuning is done using the software parameters detailed on the Dashboard screen in the Chromeleon software. 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	Use
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.	Use if Daily Tune Check fails. Follow with Daily Tune Check.
Daily Tune Check (MITC)	Checks mass, performs leak check and generates report with gain from detector sensitivity tune.	Daily

14. Quality Control

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

anomalies, corrective actions, and deviations from this SOP must be documented in the chemist's logbook, monthly QC report, and in the final data report.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Acceptance Criteria	Corrective Action
Extraction Hold Time	All samples	Store samples in freezer at ≤ 4 °C until extraction. Extract within 28 days from collection.	If hold time or temperature is exceeded, document, flag and report.
Analytical Hold Time	All sample extracts	Store extracts in freezer at ≤ 4 °C until analysis. Analyze within 28 days from extraction.	If hold time or temperature is exceeded, document and report.
Method Blank	One per extraction batch	<RL	If ≥ RL check instrument and method materials for possible contamination, reanalyze method blank and all samples in analytical batch. If the method blank is still ≥ RL, 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 blank.
Solvent Blank	One per analytical batch at a minimum	<RL	If ≥ RL check solvent, instrument, and method materials for possible contamination (i.e. carryover, solvent contamination). Reanalyze the entire analytical batch if needed. If the method blank meets criteria and there are no analytical issues, report results.
Field Blank/Trip Blank	Client request or field protocol	<RL	If ≥ RL reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Acceptance Criteria	Corrective Action
Breakthrough Analysis	One per ten samples at a minimum	No target analytes detected above RL in secondary sorbent bed	See Appendix A
Initial Calibration	Minimum of five calibration levels prior to sample analyses	$R^2 \geq 0.98$	Reanalyze. Prepare new calibration standards if criteria still not met.
Carryover Check	After analysis of a sample with MITC at or over 15 µg/mL	< RL	If the subsequent sample is <RL, no action is needed. If the subsequent sample(s) is ≥RL, reanalyze subsequent sample(s) to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. If reanalysis results meet replicate criteria, report the original result(s). If not, analyze blanks to clean system. Reanalyze samples once system is clean.
Collocated Samples	Per client request (typically 10% of field samples) or field protocol	RPD ± 25%	Verify results by reviewing data. Report results. Notify client if outside criteria.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Acceptance Criteria	Corrective Action
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 25% 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 all samples with new CCV.
Control Standard (CS)	After calibration	CS must fall within established control criteria.	Reanalyze CS. Prepare new CS if criteria still not met. Reanalyze all samples with new CS.
Replicate	One per ten or fewer samples in analytical batch	RPD ± 25%	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.

Table 4. Quality Control Corrective Actions

QC Type	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Spike (LCS)	One per extraction batch	70-130% of expected value	Reanalyze LCS and all associated samples in the extraction batch to verify results. Review all QC, document, and flag all samples in the analytical batch. Prepare and analyze a second LCS; if the second LCS and all other QC meet expected results, the original failed LCS is likely due to analyst prep error. If the second LCS also fails and all other QC passes, the LCS spiking standard should be remade. If other QC issues are present, further instrument troubleshooting is needed.
Field Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues are found.
Trip Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues are found.

15. Calculations

15.1. 0.1 percent CS_2 in EA is calculated as:

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

15.2. MITC stock standard concentration is calculated as:

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

15.3. Intermediate standard concentrations are calculated as:

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

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

$$\frac{conc.of\ intermediate\ std\ \left(\frac{\mu g}{mL}\right) x\ amount\ spiked\ (\mu L)\ x\ \left(\frac{mL}{1000\ \mu L}\right)}{5\ mL\ extraction\ volume}$$

15.5. RPD between two results is calculated as:

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

Where:

X1: first measurement value
X2: second measurement value

15.6. If EQL in µg/m³ is requested, EQL is calculated as:

$$EQL = 5\ x\ \frac{MDL\ (\frac{\mu g}{mL})\ x\ volume\ extracted\ (\frac{mL}{sample})}{sampling\ volume\ (m^3)}$$

Where:

MDL: MDL value in µg/mL units
volume extracted = 5 mL/sample for MITC
sampling volume (flow rate is 0.5 L/min): 24 hrs. = 720 liters = 0.720 m^3

15.7. Field spike percent recovery is calculated as:

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

15.8. Laboratory Control Sample percent recovery is calculated as:

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

15.9. Trip Spike percent recovery is calculated as:

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

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

$$raw\ concentration\ \left(\frac{\mu g}{mL}\right) x\ \frac{5\ mL}{sample} = \frac{\mu g}{sample}$$

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. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

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 the chemist to ensure that they were identified correctly. 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 has occurred. If shifting occurs, maintenance may need to be performed and samples reanalyzed.

16.4. The final results will be adjusted by an appropriate dilution factor and reported in µg/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 detections below the RL are not reported unless otherwise requested by the client. (i.e., certain clients or programs require 5x MDL be reported as “EQL” and concentrations between the MDL and EQL be reported as “Trace”.)

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. NLB Quality Control Manual, September 17, 2018 https://ww2.arb.ca.gov/sites/default/files/2018-10/nlbqcm.pdf

18.2. NLB Chemical Hygiene Plan, current version

18.3. NLB SOP SAS 15-01, Version 1 Standard Operating Procedure Title: Air Sampling and Analysis of Methyl Isothiocyanate (MITC)

18.4. Thermo Scientific AI 1310/AS 1310 Autosamplers User Guide

18.5. Thermo Scientific TRACE 1300 and TRACE 1310 Gas Chromatographs User Guide

18.6. Thermo Scientific ISQ Mass Spectrometer User Guide

18.7. Thermo Scientific Chromeleon 7.2 Quick Start Guide

18.8. U.S. EPA RED Fact Sheet: Methyldithiocarbamate Salts – Metam Sodium/Potassium and MITC, July 10, 2008 https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/fs_G-56_10-Jul-08.pdf

19. Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** New SOP for OLS analysis of MITC		
	July 12, 2021	MLD078 SOP for the Analysis of Methyl Isothiocyanate (MITC) in Ambient Air Using Gas Chromatography/Mass Spectrometry	NLB SOP SAS 15-01, Version 1 7/15/15. Standard Operating Procedure Title: Air Sampling and Analysis of Methyl Isothiocyanate (MITC)

APPENDIX A: BREAKTHROUGH ANALYSIS FLOW CHART