Appendix J. Chemical Analytical Method
MITC - Canisters
California Department of Health Services Laboratory

ENVIRONMENTAL HEALTH LABORATORY BRANCH
CALIFORNIA DEPARTMENT OF HEALTH SERVICES

STANDARD OPERATING PROCEDURE

Title: Methyl Isothiocyanate (MITC) by an EHLB Modified EPA Compendium Method TO-15	
Analyte: Methyl Isothiocyanate (MITC) F.W. 73.12	SOP/Rev. No: 111/RO
Matrix: Ambient Air	Date Issued: 8/30/2001
Procedure: Purge and Trap with Cryogenic focusing and GC/MS	Date Revised: 8/30/2001
	Effective Date: 8/30/2001

1. Principal and Applicability of the Method

1.1 Methyl isothiocyanate (MITC), in air, is collected in an evacuated silanized stainless steel canister. A portion of the sample is processed using a cryogenic purge and trap technique for GC/MS analysis. The MITC molecule is separated and subsequently fragmented for identification and quantification.

1.2 This MITC analysis is a modification of the EPA TO-15 Method for volatile organic compounds (VOC). The use of the "Cold Trap Dehydration" purge and trap is necessary to eliminate significant interference from water present in ambient samples.

1.3 The modified Method (TO-15) requires the analyst to have specialized skills to successfully quantitate for MITC. The analyst should be familiar with both static and dynamic gas dilution techniques to prepare different MITC concentrations (in canisters) from either a stock neat liquid standard or a certified gas cylinder. The analyst must also be knowledgeable in GC/MS analysis to quantitate MITC in air samples.

1.4 This method utilizes both the "purge and trap" technique and the capillary column chromatography to mitigate interference from ambient water present in the sample. Single ion monitoring is employed to reduce the detection limit for this compound.

2. Range and Sensitivity

2.1 The range and sensitivity is dependent on the mass spectrophotometer's scanning method used. Low MITC concentrations warrant using single ion monitoring (SIM) for better sensitivity. Using SIM with mass numbers unique to MITC in conjunction with a retention time window for the DB-wax column provides specificity superior to typical gc/NPD detector.

2.2 This method has a practical calibration range from about 0.024 to about 2.39 nanograms of MITC for a 400 cc sample volume. This equates to sample concentrations of 0.020 and 2.0 ppbv.

2.3 The "method detection limit (MDL)" is calculated from the product of the Student's t value (at the 99 percent confidence level) and the standard deviation. The standard deviation is derived from at least seven (7) replicate determinations of the lowest (expected) concentration limit achievable.

2.4 The "reporting limit" or method quantitation limit (MQL) is three times the MDL.

3. Safety Considerations

3.1 All analysts must adhere to the EHLB Health and Safety regulations.

3.2 Methyl isothiocyanate is toxic. The analyst may be working with high MITC concentrations in organic liquids and in compressed gas cylinders. All preparative work, including static and dynamic gas dilutions, is performed in the fume hood following good standard laboratory and specialized gas handling techniques.

3.3 Working with MITC at high ppm levels in compressed gas cylinders presents special precautions and emergency protocols. If high ppm levels of MITC gas mixtures are accidentally vented into the laboratory-mandated evacuation of the laboratory may be in order.

4. Interferences

4.1 No significant interferences are known at this time. Purge and trap conditions must be set to minimize water transfer to the gc/ms. Note that residual water purged from the solid sorbent traps (of the cryofocusing unit) can significantly affect the retention time of MITC.

5. Equipment and Supplies

5.1 Mass spectrometer: Finnigan 4500 EI/CI (or equivalent)

5.2 Gas chromatograph: Varian Star Model 3400 (or equivalent)

5.3 Fused silica capillary column--30 meters by 0.25 mm I.D. by 0.25 micron film thickness: DB-Wax.

5.4 Purge and trap/ cryogenic focusing module: Entech 7000 (or equivalent)

5.5 Canister cleaning system: Entech 3000 (or equivalent)

5.6 Standard preparation system with mixing chamber: Entech 4560 SL (or equivalent)

5.7 Passive Flow Controller with a twenty-four (24) hour restrictor: Entech CS 1200 (or equivalent)

5.8 Pentium III based PC and a Windows 98/NT operating system to control the GC/MS and Enteck 7000 systems.

5.9 Glass vials with Teflon lines caps. 8 and 25 mL amber vials.

5.9 Liquid syringes with Teflon plunger: 5 uL, 10 uL, 25 uL, and 100 uL capacities:

Note: All volumes dispensed from the above syringes shall be greater than or equal to 40 % of the maximum capacity. Any syringes not listed must adhere to this 40 % rule. Syringes should be calibrated.

5.10 Class "A" pipettes: 1 and 10 mL volumes.

5.11 6 Liter Silcocanisters (with Silianized interior coating).

5.12 Analytical balance: Mettler AT400 (or equivalent).

5.13 Bubble Meter: Hasting (or equivalent).

5.14 Mass Flow Controller 0 – 500 ccm range: Matheson (or equivalent).

5.15 Mass Flow Controller 20 – 1000 ccm range: Matheson (or equivalent).

5.16 A purge chamber, containing HPLC grade water, glass beads and topped with glass wool, is used to humidify zero air. The water level is between half and ¾ of the glass bead volume and never touches the glass wool. The water must be gently boiled and purged with helium or nitrogen for at least 4 hours to eliminate dissolved organic compounds.

5.17 Gas tight syringe-10 mL capacity.

5.18 Heated injector: A split-less gc injector wrapped with an electrical heating tape. A variable autotransformer (Power stat) controls the heat generated to the injector. A thermocouple is used to measure the external temperature of the injector

5.19 Entech pressure sensor (or equivalent): 0 to 50 psia.

6. Reagents and Standards

6.1 Methyl isothiocyanate: Primary source: greater than 95 % purity as certified by manufacturer's statement of analysis.
6.2 Hexane: Pesticide grade or equivalent.
6.3 High purity zero air: 99.999 or better.
6.4 High purity nitrogen gas: 99.999 or better.
6.5 Liquid nitrogen.
6.6 Helium: 99.9999 or better equivalent.
6.7 Methanol: Pesticide grade or equivalent.
6.8 Finnigan 4500 Calibration and Tuning Compound: Perfluorotributylamine.
6.9 4-Bromofluorobenzene: EPA TO-15 GC/MS Tuning Compound. Ordered premixed with certification as to a) concentration, b) percent purity, c) GC chromatogram, d) expiration date, e) lot number, and f) solvent used for dilution (same solvent should be used for further dilution). Once opened, the useful life is not to exceed one year.

6.11 Standard Preparation:

Both the Dynamic and Static techniques can be used to prepare MITC standards. The Dynamic technique allows the analyst to prepare a standard for direct injection into the cryofocusing unit for analysis and/or into a silcocanister. With the Dynamic technique, the pressure across the cyrofocusing unit's mfc is constant regardless of the volume size taken for analysis. This is not true with canisters, as the pressure will drop significantly with increase sample volume. As more and more sample volume is taken, the pressure differential across the cryofocusing unit's mass flow controller will change. This change can be dramatic if more than 1 to 1.5 liters are taken. With this change in the pressure differential, the mass flow controller may not accurately dispense the require sample volume. Hence, using standard canisters to prepare a calibration curve would be better suited for analysis of sample canisters. Since the calibration range of 0.020 to 2.0 ppbv, and the MDL of 0.015 ppbv were determined from standards prepared using the Static technique, then the Static technique is recommended to achieve the MDL and calibration range.

6.11.1 Static Standard Preparation Technique.

Generally, a volume of MITC standard in hexane is injected through a septa onto a heated gc injector at ambient pressure. The heated neat standard is purged with a humidified gas into the evacuated silcocanister over time. The measured flow time and the dilution gas flow rate together yield the total dilution gas volume. With the known MITC mass and total dilution gas volume, the actual MITC concentration can be calculated at the known relative humidity of the dilution gas. The following is the procedure used for the Static Standard Preparation Technique.

The inside of the cooled injector is rinsed with hexane. The injector is then heated and purged at a flow rate near one liter per minute with dilution gas for not less than 30 minutes. This cleaned injector needs to be validated by filling a clean canister with zero air or nitrogen through the heated injector for GC/MS analysis to check for contamination.

The primary MITC neat liquid standard is prepared by dissolving MITC in hexane. Micro-liter quantities of this standard are injected through a septum into a stand alone heated injector at 130 degree centigrade and at atmospheric pressure.

If the heated injector is pressurized, the neat solution could be pushed up the syringe barrow. If the injector is under vacuum, the excess neat liquid within the syringe needle could be withdrawn into the canister. The injector's must be at ambient pressure during injection of the standard neat solution.

A known volume of 50% RH diluent gas is subsequently used to purge the MITC into a 6 liter evacuated canister. Fill the canister to the target volume with the dilution gas. If the canister needs to be pressurized, insure that the canister pressure is less than 35 psia, and replace the septa with a new one to prevent leaks (if needed).

50% RH air is prepared by blending equal flow rates of 100% humidified air with dry air. Set up two mass flow controllers (MFC) to deliver the gases at the same flow rate of approximately 200 ccm. One MFC will control the flow of the dry gas stream. A second MFC will control the flow of dry gas purged through a bed of glass beads in water.

Flow rates for both MFCs are calibrated with a NIST traceable bubble meter.

Inject the neat stock standard solution into the injector. Turn the vent valve (on the heated injector) to divert air into the canister. Immediately note the time and open the silcocanister valve. Air (dilution gas) should flow through the repository until the required volume is reached. The exact elapsed time is calculated from the total dilution volume needed divided by the measured airflow rates.

Calculated fill time: (Target volume in Silcocanister)/(Total humidified airflow)

For example at 50% RH: (6000 cc)/ (200 dry gas cc/min + 200 humidified gas cc/min) = 15 minutes

Finally, shut off silcocanister valve when the calculated fill time has been reached.

Keep the total dilution gas flow below 1000 ccm. A lower flow rate would require longer fill times which translates to better accuracy and precision results because there is better control of the dilution gas volume. A 400-ccm flow rate is recommended to prepare standards requiring 15 minute fill time for a 6 liter canister.

An example of a preparation of a 0.33 and1.0 ppbv standards:

Target Conc ppbv	1^0 MITC Std in Hexane Conc: ng/uL	Vol Std Injected uL	2^0 MITC Std in Hexane. Volumetric Flask Used mL:	Volume taken from 2^0 Std uL	Dilution Gas Fill Vol L	Fill Time Minutes @ 722.5 ccm Total Flow	Final MITC Conc ppbv
0.33	10000	4	50	6.2	5.3	7.34	0.32
1.0	10000	4	25	9.5	5.3	7.34	0.96

Note: Instead of the neat liquid MITC standard, injection of MITC certified gas standards with gas tight syringes can be substituted for the above liquid neat standard.

6.11.2 Dynamic Standard Preparation Technique:

This technique prepares analytical standards by blending known volumes of a certified gas standard and a dilution gas together. The gas volumes are calculated from the calibrated mass flow controllers used to dispense a certified MITC standard and humidified dilution gas into a mixing chamber. The resulting mixture can be used to fill canisters for standards.

Certified MITC cylinders may not be stable in gas cylinders over a period of months, and requires that the certified gas standard be analytically assayed before used.

This technique is applicable when the target concentration requires a certified standard gas volume near 100 cc or higher for subsequent dilution. However, low flow rates can be used if the following procedure is also followed.

A mass flow controller, set to deliver low flows (1 to 10 ccm), is calibrated to deliver a known volume from the standard gas cylinder over several minutes (ideally greater than 10 minutes). The certified standard gas is added to the canister before filling the canister with the humidified dilution air. Large certified standard gas volumes used can change the % RH in the canister and flow adjustments of dry and 100% humidified dilution gases should be made to attain the target %RH value.

See Section 6.11.1 to generate 50% RH air for dilution of the standard gas.

Example:

MITC gas standard:	10 ppm (equals 10 uL / L or 10,000 nL / L)
Target MITC conc.:	10 ppbv (or 10 nL / L)
Volume of Silcocan:	6 L
Total Volume of MITC STD:	6L times 10 nL / L (or 60 nL needed)
10 ppm MITC volume required:	(1000 mL / 10,000 nL)(60 nL) or 6 mL

MITC MFC set at 1 ccm: to get 6 mL, the MFC needs to be switched on for six minutes.

For 50 % RH zero air, set the two MFC to deliver a 200 ccm each. As in Section 6.11.1 above, the fill time should be 15 minutes.

Calculation:

10ppbv MITC =

((10,000 ppbv)(1ccm)(6 min))/((200ccm*15 min)+(200ccm*15 min)+(1ccm*6 min))

Note: For small volumes, the use of gas tight syringe (with 10 cc capacity) to add the *standard is recommended (Static Method). The MFC (used for very low flows) needs to* be preconditioned by passing the standard through it for at least half an hour.

6.11.3 Methyl isothiocyanate stock standard (10mg/mL)
<u>Discard after 6 months</u>

Weight out 50 mg (approximately) of methyl isothiocyanate into an 8 mL amber vial. Dispense 5 ml of hexane and seal with Teflon lined cap.

Label each vial with:

a) Date of Preparation
b) Date of Expiration
c) Concentration in solvent
d) Initial of analyst who prepared standard

6.11.4 4-Bromofluorobenzene: EPA TO-15 GC/MS Tuning Compound: Canister
<u>Discard after two months or as needed</u>

a) Preparation of BFB 2^0 Standard at 333 ug / mL (or ng / uL) by

adding 200 uL of the 1^0 BFB Standard into a vial containing 1 mL of methanol.

b) Inject 9 uL of the 2^0 Standard into the 6-liter Silcocan by the Static Standard Preparation Technique (6.11.1). This yields 50 ng / 100 cc of sample.

c) Fill the six liter canister with 50% RH zero air as in Section 6.11.1.

Needed BFB for GC/MS tuning:	50 ng / analysis
Analytical sample volume:	100 cc / analysis
Entech 7000 Method:	Micro scale purge and trap.
4-Bromofluorobenzene conc.	2000 ug / mL (or ng / uL)
Silcocan Volume:	6000 mL
Needed BFB / 6L Silcocanister:	(6000/100)*50 ng =3000 ng

The BFB tuning compound is very stable and a new standard only needs to be prepared when the canister pressure is very low (about 10 psia for a 6 L canister).

6.11.6 Canister: Calibration curve standards
Discard after two weeks or sooner

Depending on the purge and trap instrument used, no more than 1200 cc should be taken from each canister (filled to 5 to 6 L) for the calibration curve. Below this volume, the vacuum pump may not be able to precisely withdraw more sample volume from the canister. The net result is that the calibration curve is not accurate.

Three canisters are used to generate a multipoint calibration curves. Canisters prepared at 0.1, 0.33, and 1.0 ppbv concentrations should be prepared to span a concentration range of 0.03 to 1.6 ng of MITC:

MITC Canister Conc: ppbv	Volume Analyzed: mL	Nanograms analyzed
0.1	100	0.03
0.1	200	0.06
0.1	400	0.12
0.33	200	0.20
0.33	400	0.39
1.0	200	0.60
1.0	400	1.20
1.0	533	1.59

For samples with high MITC levels beyond this calibration curve, reanalyze with less sample volume. In this method, no less than 100 mL sample volume will be used (this is twice the manufacturer's minimum). Otherwise, prepare three canisters that will bracket the sample concentrations, and prepare a QCH and QCL that are 75% and 25% of the highest standard prepared respectively.

6.11.7 Canister: Field Blank (FB) Sample
Maximum Hold time: 2 weeks after receipt

Prepared by filling the 6 Liter Silcocanister with 50 % RH zero air (by-pass the injector to eliminate contamination problems).

6.11.8 Canister: Field Spike (FS) Sample
Maximum Hold time: 2 weeks after receipt

Field Spike Target Concentration:	1.0 ppbv MITC in 50% RH zero air.
Field Spike Preparation Technique:	Static injection (Per Section 6.11.1) of the Secondary Standard in 50 % RH Zero Air.

6.11.9 Canister: EPA TO-15's Daily Calibration Standard: 1.0 ppbv
Discard after 2 weeks

This is a second canister different from the one used for the calibration curve. The daily calibration standard is used if the calibration curve is not updated.

6.11.10 Canister: Audit Sample: 1.0 ppbv MITC in 50% RH air
Discard after 2 weeks

See Section 6.11.1 above for the preparation of a 1.0 ppbv audit sample.

6.11.11 Canister: EHLB's Quality Control Samples: 0.33 and 1.0 ppbv
Discard after 2 weeks

See Section 6.11.1 above for the preparation of the QC high and low samples.

6.11.12 Laboratory Method Blank (LMB)
Discard after 2 weeks

Prepared as in Section 6.11.7 above.

7. Sample Collection, Preservation, Shipping, and Storage

7.1 Sample collection.

7.1.1 Prior to sample collection all Silcocanisters used must be cleaned. The canisters are heated during a cycle, which includes evacuation to 150 mTorr and refill to 30 psia.for two cleaning cycles. The third and final cycle has a final evacuation to $\leq$ 50 mTorr.

For storage, the canisters are filled to 30 psia with ultra pure humidified nitrogen 50% RH). Before evacuation for sampling, store canisters are leak checked to see if the pressure is within +/- 2 psia of the initial pressure.

Each of the cleaned canisters are analyzed by GC/MS to determine the blank level. MITC must be below the MDL or the canister must be cleaned again as detailed above.

For sampling, canisters are evacuated to $\leq$ 50 mTorr and sealed with a Swagelok cap. The caps should be tightened with a wrench.

7.1.2 Chain of Custody form is signed before transferring both canisters and the passive flow controllers. Custody seal is to be included for each canister.

7.1.3 Silcocanisters are shipped to the sampling site by ground transportation in a protective shipping container. Chain of Custody must document transfer of the samples to the carrier and be included with the samples for transportation.

7.1.4 Just prior to sampling, remove the Swagelok caps from both the canister and the Entech CS 1200 flow regulator. Attach the Entech CS 1200 flow regulator to the inlet of the canister, and tighten the Swagelok connection with a wrench. Record the identification numbers of Silcocanister and the Entech CS 1200 flow controller. Record the relative humidity, ambient temperature and pressure, and sampling location.

To begin sampling, remove the soft rubber cap from the inlet of the CS 1200 flow controller and pull out the steel pin (if present) to turn the canister valve on (1/4 turn and vertical up). Record the start time and initial canister vacuum indicated by the flow controller gauge.

To stop sampling, close the valve and lock in place with the steel pin. Record the stop time, relative humidity, ambient temperature, vacuum (with a pressure gauge), and final flow rate (with a rotometer or equivalent) just before the end of the sampling period.

Remove the flow regulator from the canister and cap the silcocanister. Tighten cap with a wrench for transport in the designated shipping container. Finally, cap the CS 1200 at both ends for transport with the canister.

Note and record on the chain of custody any observations, which may have an impact on sampling---such as heavy traffic, rain, fog, smog, and other factors-which might affect the analytical results.

7.1.4 Upon receipt in the laboratory the chain of custody is signed and the analyst will log in the samples into the EHLB internal sample tracking system.

7.2 Maintain the canisters at a constant ambient temperature. Do not cool.

7.2.1 The sample holding time shall be a maximum of 2 weeks.

8. Quality Control

8.1 Each sample is given its own unique sample batch identification number following EHLB labeling protocol.

8.2 Each batch shall include the following QA/QC samples (in 50% RH air):

a) Field and a laboratory (methods) blanks.

Sections 6.11.7 and 6.11.12

b) Field and a laboratory QA/QC samples.
Sections 6.11.8 and 6.11.11

c) *Audit sample (if available): could be duplicate field and laboratory samples.*
Section 6.11.10

8.3 The QC Low and QC High samples are prepared as described in Section 6.11.11. Both QC samples are to be analyzed for each batch of samples. However, only one of the low or high QCs is analyzed with each 10 samples within the batch.

Note: The QC Low and High samples are used to generate the QC chart. Typically, 400 cc are used per analysis.

8.4 A Control Chart will be maintained with the limits defined in the EHLB QA/QC quality assurance manual, which states that analysis is in control when the QC results are within +/- 2 standard deviations, and out of control beyond +/- 3 standard deviations.

9. Calibration and Standardization

9.1.1 Flow Controller Calibration

9.1.2 Each Entech CS 1200 passive flow controller (PFC) is calibrated using an evacuated 6-liter canister to draw ambient air through the PFC until the pressure rise causes the flow to change significantly.

9.1.3 Calibration of the PFC Uses a calibrated electronic mass flow controller (1 to 20 ccm), a three way ¼" Swagelok valve, 6 liter canister, and a vacuum pump. The three-way valve is used to evacuate the canister or to allow air to flow from the PFC into the canister.

9.1.4 The mfc is calibrated using a NIST traceable Hastings Bubble Meter or an equivalent flow calibration device. Record the ambient temperature and pressure to reduce the flow to standard conditions if needed.

9.1.5 The electronic mass flow controller (mfc) is connected to the inlet of the PFC. The "air flow" goes from the mfc through the PFC and into the canister. Flow measurements are taken from the mfc's digital display at a specific PFC gauge reading.

9.1.6 Turn the "three way" valve to pull air from the PFC into the empty canister. With the electronic mass flow controller connected to the PFC, turn the PFC's "flow adjustment screw" until the desire sampling flow rate is displayed on the mfc. Turn the "three way" valve off to allow the PFC to reach ambient pressure to properly seat the PFC. Draw air through the PFC again to verify the set flow—otherwise, adjust again and allow the PFC to return to ambient pressure and check flows again. Repeat until display flow is within +/- 10% of target flow at gauge pressure near -25 "Hg. Other wise, do not use this PFC.

9.1.7 Turn switch on the three way valve to evacuate the canister. When the pressure reads about –25 "Hg, turn the valve to pull air through the PFC and read the flow off the electronic mass flow controller. As the canister pressure increases, take measurements at different pressure intervals to relate canister pressure vs. flow reading.

9.1.8 Record the ambient pressure and temperature to reduce the flow determinations to sccm.

9.1.9 Maintain a log book on each Entech CS 1200 identified by a serial number. Include the date when the controller's sintered glass filter was changed, the controller was calibrated, and the canister attached for sampling.

9.2.1 Instrument Calibration

9.2.2 For the Finnigan GC/MS, perfluorotributylamine is used to tune the mass spectrometer daily

9.2.3 100 mL of the bromofluorobenzene TO-15 tuning standard (Section 6.11.3) is trap using the Enteck's Microscale Purge and Trap method to check the tune of the mass spectrometer. If not within specifications as shown in EPA TO-15 Table 3, repeat 9.4 to retune and reanalyze the BFB tuning compound.

9.3 A standard curve can be obtained by taking known volumes from the calibration standard as in described Section 6.11.6.a.

9.4 Once yearly or more often, check the flow rate of the Enteck 7000 mass flow controller. Contact Enteck to reset the Enteck calibration setting to match actual flows.

10. Analytical Procedure

Pre-sampling

10.0 Clean each passive flow controller as follows.

a) Remove the sintered glass filter from the critical orifice.
b) Follow manufacturer's cleaning procedure to clean the internal surfaces making sure that the internal pressure does not excess 3 psig.
c) Use clean air or nitrogen that has been scrubbed with a hydrocarbon filter.
d) Replace the sintered glass filter with a new one or one certified as clean.

10.1 Check the Entech CS 1200 passive flow controller calibration before sending it out for sampling as follows:

a) Cap (with Entech's black rubber cap) the open sampling port of the PFC controller and apply a firm pressure with your thumb over the cap. Apply vacuum close to -25 "Hg, and note if the pressure increases quickly due to a leak once the vacuum is switched off completely isolating the PFC. If the gauge reading does not increases over two minutes, the CS 1200 probably does not have a major leak. Do not use unless leak has been isolated and fixed.

b) Set up a pump to draw air through a calibrated electronic mass flow controller to measure the passive flow controller's sampling rate. The CS 1200 controller flow should be within +/- 10 % of the electronic mass flow controller's calibrated range.

c) Store the PFC in their own shipping boxes for transportation along with manufacturer's operating instructions.

10.2 Evacuate all canisters that have been blank checked for contamination and pressure checked for leaks for at least 24 hours. Capped the canisters and tighten with a wrench.

Sampling Deployment

10.3 Transfer the canisters into the shipping container(s) along with custody seals and the CS1200 passive flow controllers.

10.4 Prepare the trip blank, trip spike, to be ship with the sampling canisters no earlier than 24 hours before being shipped.

10.5 Prepare the laboratory blank, and laboratory spike at the same time as the trip blank and lab spikes are to be retained under locked storage.

10.6 Prepare a chain of custody form to include the canisters and CS 1200s.

10.7 Transfer the canisters and PFC to the appropriate sampling team member or ship canisters. Sign off on the shipping document and include that document along with the samples.

10.8 Include notice that the samples must be shipped back as soon as possible due to a hold time of 14 days after sampling.

Analysis

10.9 After sampling, take custody of the samples and sign off on the chain of custody form. The analytical laboratory retains the original and a copy is given to the client.

10.10 Store the samples in a locked cabinet or a secure room.

10.11 For each 24-hour of analysis, prepare the three standard canisters as outlined in Section 6.11.6, QCL (0.33ppbv) and a QCH (1.0 ppbv) as in section 6.11.11 above.

10.12 Set up the Entech 7000 cryofocuser sequence file and Galwin 98 "GC/MS" sequence file to include the analytes in the following order using the Entech 7000 "CTD" method (except for BFB).

a) BFB: Abort sequence if this does not pass (Use MPT "Section 10.14.1").
b) Eight point calibration curve.
c) QCL and QCH
d) Laboratory Blank air or nitrogen
e) Samples: set of 5 and 5 for a total of 10 samples
f) QCL and QCH
g) Two replicates

10.13 MITC sample Analysis "Cold Trap Dehydration" Cryogenic Parameters (Entech 7000 or equivalent):

Trap One (Glass Beads—Module 1)

a)	Trap Temp:	-20 °C
b)	Sample Preflush:	50 cc/min for 5 sec.
c)	Sample Flow Rate:	50 ccm
d)	Trap Preheat Temp:	20 °C
e)	Desorb Temp:	100 °C
f)	Sweep gas Preflush:	50 cc/min for 2 sec.
g)	Sweep Rate/Total Vol:	50 cc/min to 50 cc
h)	Trap Bake Parameter:	130 °C for 25 mins.
i)	Bulk Head Control	
	1)Trap:	30 °C
	2) Desorb:	110 °C
	3) Bake:	130 °C

Trap Two (Tenax—Module 2)

a)	Trap Temp:	-40 °C
b)	Desorb Temp:	180 °C
c)	Module 1 to 2 Sweep:	10 cc/min to 10 cc total volume
d)	Module 2 bake:	190 °C for 6 minutes
e)	Bulk Head Control	
	1) Trap:	30 °C
	2) Desorb:	110 °C
	3) Bake:	100 °C

Trap Three (Cryofocuser—Module 3)

a)	Trap Temp:	-150 °C
b)	Inject Time:	2 minutes

10.13.1 BFB tuning calibration "Microscale Purge and Trap" Cryogenic Parameters (Entech 7000 or equivalent):

Trap One (Glass Beads—Module 1)

j)	Trap Temp:	-150 °C
k)	Sample Preflush:	50 cc/min for 5 sec.
l)	Sample Flow Rate:	50 ccm
m)	Trap Preheat Temp:	20 °C
n)	Desorb Temp:	20 °C
o)	Sweep gas Preflush:	100 cc/min for 2 sec.
p)	Sweep Rate/Total Vol:	100 cc/min to 75 cc
q)	Trap Bake Parameter:	130 °C for 15 mins.
r)	Bulkhead Parameters:	
	1) Trap:	30 °C
	2) Desorb:	30 °C
	3) Bake:	130 °C

Trap Two (Tenax—Module 2)

a)	Trap Temp:	-40 °C
b)	Desorb Temp:	180 °C
c)	Module 1 to 2 Sweep:	10 cc/min to 10 cc total volume
d)	Module 2 bake:	190 °C for 6 minutes
e)	Bulkhead Parameters:	
	1) Trap:	30 °C
	2) Desorb:	100 °C
	3) Bake:	130 °C

Trap Three (Cryofocuser—Module 3)

a) Trap Temp:	-150 °C
b) Inject time:	2 minutes

10.14 Tune the Finnigan mass spectrometer according to manufacturer's procedures with Perfluorotributylamine ($[(CF_3(C_3F_6)]_3N$). Check for air leak in the GC/MS.

10.14.1 The Galwin 98 gas chromatography parameters (for BFB analysis):

Initial conditions: Column at 35 ^{0}C, Injector at 100 ^{0}C, and Detector at 200 ^{0}C.
Program mode: Initial hold time at 1 minute at 35 ^{0}C, Ramp to 200 ^{0}C at 10 ^{0}C/min,
Final Hold time 15 minutes at 200 ^{0}C.
Helium pressure is 11 psig
Capillary flow rate is 1 ccm.

Mass Spectra Scan Method: Full Scan

Filament Delay: 360 seconds
Scan Time: 9 minutes)

10.14.2 The gas chromatography parameters for all analytes:

Initial conditions: Column at 35 ^{0}C, Injector at 100 ^{0}C, and Detector at 200 ^{0}C.
Program mode: Initial hold time at 1 minute at 35 ^{0}C, Ramp to 100^{0}C at 10 ^{0}C/min,
Ramp to 200 ^{0}C at 20 ^{0}C/min
Final Hold time 1 minutes at 200 ^{0}C.
Helium pressure:
Flow rate:

Mass Spectra Scan Method: Single Ion Monitoring

Filament Delay: 360 seconds
Scan Time: 9 minutes

10.15 Check the BFB fragmentation pattern when acquisition is complete. Compare the results with the table below.

BFB Fragmentation Specifications

Mass Number	Base Peak Reference	Minimum % Intensity	Maximum % Intensity
50	95	8.0	40.0
75	95	30.0	60.0
95	Base	100.0	100.0
96	95	5.0	9.0

173	174	0.0	2.0
174	95	50.0	120.0
175	174	4.0	9.0
176	174	93.0	101.0
177	176	5.0	9.0

10.15.1 If the BFB tune fails after samples have been analyzed, retune MS with FC43 and analyze BFB again. If BFB passes, run sequence according to Section 10.12.

10.16 At the conclusion of a sequence run, identify samples with concentrations of 10 ppbv or higher. If any are found, reanalyze the sample following it to check for carry over.

10.17 Identify samples that have concentrations exceeding the calibration curve. Reanalyze these samples using smaller volumes or diluted for reanalysis. See Section 6.11.13.

11. Calculations and Reporting

The required calculations are in EPA Compendium Method TO-15 (EPA/625/R-96/010b) Section 10.5.4.

The EPA section covers: Response Factors, %RSD, Retention Times, Acceptance Criteria, and Corrective Actions. Note, that no internal standard is used and the calculations apply to mitc area counts only.

12. Data Assessment and Acceptance Criteria

QUALITY CONTROL DESCRIPTION	FREQUENCY	ACCEPTANCE LIMIT(S)
Calibration Verification Blank (EHLB's Continuing Calibration Verification Blank [CCVB]): (See Section: 6.11.7)	Once per 24 hour run and after samples with 10 ppbv or higher concentrations.	Less than 0.02 ppbv (MDL)
Laboratory Method Blank (EHLB's Method Blank [LMB]): (See Section: 6.11.12)	Once per Batch	Less than 0.02 ppbv (MDL)
Field Blank (EHLB's Field Blank [FB]): (See Section: 6.11.7)	Once per Batch	Less than 0.02 ppbv (MDL)
Daily Calibration Standard (Initial Calibration Verification Standard [ICVS]): (See Section: 6.11.9)	Once per 24 hour run if no new calibration curve is generated.	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviation.
Quality Control Standards (EHLB' Continuing Calibration Verification Standard [CCVS]): (See Section: 6.11.11)	Once per each 10 samples / 24 hour run	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviation.
Field Spike (EHLB's Field Spike [FS]): (See Section: 6.11.8)	Once per Batch	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviations.
EPA Audit Sample [AS]: (See Section: 6.11.10)	Once per Batch (if submitted)	Per EPA TO-15 Section 11.4.1 +/- 30 percent.
Instrument Performance Check Standard [IPCS]: 50 ng BFB: (See Section: 6.11.4)	Once / 24 hour run	Per EPA TO-15 Section 10.4.3 For Selected ion.
Internal Spiking Standard [ISS] In 50 % RH zero air: (See Section: 6.11.5)	With each determination (if used)	Per EPA TO-15 Section 10.7.5 +/- 40 % of Mean area response; retention time within +/- 0.33 minutes.

13. *Corrective Actions*

QUALITY CONTROL DESCRIPTION	ACCEPTANCE LIMIT(S)	CORRECTIVE ACTION
Calibration Verification Blank (EHLB's Continuing Calibration Verification Blank [CCVB])	Less than 0.02ppbv	Purge Entech 7000 purge and trap system out until acceptable. Report results of this analysis.
Laboratory Method Blank (EHLB's Method Blank [MB])	Less than 0.02 ppbv	Purge Entech 7000 purge and trap system out until acceptable. Report results of this analysis.
Trip Blank (EHLB's Trip Blank [TB])	Less than 0.02 ppbv	Report the results of this analysis. Determine source of contamination.
EPA's Daily Calibration Standard (Initial Calibration Verification Standard [ICVS])	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviations.	Generate another calibration curve until ICVS result is acceptable.
Quality Control Standard (EHLB' Continuing Calibration Verification Standard [CCVS])	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviations.	Generate another calibration curve and reanalyze samples from the previous passing CCVS.
Field Spike (EHLB's Field Spike [FS])	See EPA TO-15 Section 8.4.4.9 Results acceptable within +/- 3 standard deviations.	Report the results of this analysis. Determine the source of the problem. Report findings.
EPA Audit Sample [AS]	Per EPA TO-15 Section 11.4.1 +/- 30 percent.	Report the results of this analysis. Determine the source of the problem. Report findings.
Instrument Performance Check Standard [IPCS]: 50 ng BFB	Per EPA TO-15 Section 10.4.3 For Selected ions.	Retune and run last 2 samples and QCs. If results are not within 1 standard deviation, reanalyze the last 10 samples.
Internal Spiking Standard [ISS] In 50 % RH zero air: If used.	Per EPA TO-15 Section 10.7.5 +/- 40 % of Mean area response of current calibration curve; retention time within +/- 0.33 minutes	Retune and run last 2 samples and QCs. If results are not within 1 standard deviation, reanalyze the last 10 samples.

14. Method Performance

14.1 Accuracy and precision:

9 replicate determinations of a standard at 0.030 ng yielded a mean of 0.032 ng with a Standard Deviation of 0.005 ng.

14.2 Accuracy and precision control limits:

Accuracy and precision control limits are +/- 2 standard deviations of the quality control samples, and out of control beyond +/- 3 standard deviations.

14.3 Method Detection Limit and Reporting Limit:

a) Method Detection Limit: 0.015 ppbv or 0.018ng total mass
Based on 400 cc sample volume.

b) Method Reporting Limit: 0.045 ppbv or 0.054ng total mass
Based on 400 cc sample volume and three times the MDL.

15. Waste Management

15.1 Samples in canisters to be cleaned by heated evacuation and flushing with nitrogen using the Entech 3000 or equivalent (See Section 7.1.1)

15.2 Standards and Reagents are discarded in a labeled waste container to be discarded through the department's hazardous waste disposal contractor.

16. References

EPA Compendium Method TO-14a, "Determination Of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography"

EPA Compendium Method TO-15, "Determination Of Volatile Organic Compounds (VOCs) In Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"

17. Approvals

Prepared by: _____ *Date:*

Reviewed by: _____ *Date:*

Approved by: _____ *Date:*

ENVIRONMENTAL HEALTH LABORATORY BRANCH
CALIFORNIA DEPARTMENT OF HEALTH SERVICES

STANDARD OPERATING PROCEDURE

Title: **Methyl Isothiocyanate Determination in Air by Charcoal Sorbant Tubes**	
Analyte: Methyl Isothiocyanate (CAS 556-61-6)	SOP/Rev. No: 112/RO
Matrix: Ambient Air	Date Revised: 8/30/2001
Date Issued: 8/30/2001	Effective Date: 8/30/2001

1. Principle and Applicability of the Method

1.1 This method measures Methyl Isothiocyanate (MITC) in air. Sampling is performed using charcoal sorbent tubes. The charcoal is desorbed in ethyl acetate/CS_2, and the analyte is analyzed by gas chromatography with a Nitrogen-Phosphorus detector (GC-NPD).

1.2 The method is applicable for the determination of MITC in air ambient air samples.

2. Range and Sensitivity

2.1 The calibration range is 30 to 3000 ng/3mL desorbant (0.1% CS_2 in ethyl acetate).

2.2.The Method Limit of Detection (MDL) is 12 ng/sample (based on spiked charcoal extracted samples).

3. Safety Considerations

3.1 The analyst will follow the safety procedures stated in the Environmental Health Laboratory Branch Health and Safety Manual.

4. Interferences

3.2 Humidity can affect the collection efficiency. No interferences have been observed.

5. Equipment and Supplies

5.1 Gas chromatograph with a nitrogen-phosphorus(NPD) detector and split-split-less injector Agilent 6890 (or equivalent).
5.2 Capillary column, J & W DB-5, 30 m, 0.25 mm i.d.& 1.0.um film thickness
5.3 Autosampler: LeapCTC A200SE , Agilent 7683 (or equivalent).
5.4 Data System: HP Chem Station (or equivalent).
5.5 .Carrier gas: Helium, 99.999% purity.
5.6 Make-up gas Nitrogen 99.999%
5.7 Air: ultra-zero.
5.8 Hydrogen ultra pure.
5.9 GC gas flow measuring device.
5.10 Analytical balance.

5.11 Explosion-proof refrigerator for storage of standards and CS2..
5.12 Explosion-proof refrigerator (not the same one as for standards) for storage of desorbed samples.
5.13 Glassware & related items: volumetric flasks, TD volumetric pipettes; 5 ¼ in. glass disposable Pasteur pipettes Pasteur pipettes, one dram (4 mL) vials with teflon septa for samples , several 2 dram (8 mL)vials for stock standards, auto septa vials with septa caps and solid caps for sample storage.
5.14 Syringes: 10ul
5.15 Coconut charcoal sorbent tubes: SKC cat. No. 226-09, 8 x 100 mm, 200/400 mg. Use the same lot number for all analysis.
5.16 Developing Vial vibrator and vial racks.
5.17 Charcoal tube tools: scribers, glass-wool pullers.

6 Reagents and Standards

6.1 All reagents should be certified pure with a certificate of analysis.

6.2 Ethyl Acetate, Mallinckrodt Chrom AR-HPLC (or equivalent).

6.3 Carbon Disulfide, low Benzene grade, CEM OmniSolve cat. # CX-0397-6, 500 mL size (or equivalent).

6.4 Toluene, CEM OmniSolve (or equivalent).

6.5 Methyl Isothiocyanate (mitc). Aldrich, purity 97% Store in refrigerator not freezer according to manufacturer's recommendations.

7 Sample Collection, Shipping , and Storage

7.1- Chain of Custody: Client will initiate the chain of custody form with consultation with EHLB to include all needed sample information. A copy of the chain of custody is to be retained by EHLB and the original kept with the samples.

7.1 The EHLB transfers the charcoal tubes for samples and all blanks and quality assurance spikes as follows:

a) Trip Blank
b) Trip Spike Low (1000 ng/ tube)
c) Trip Spike High (3000 ng/ tube)

7.2 Sample Collection

7.2.1 Sampling protocol to be established by the contracting agency.
7.2.2 This method is based on a 2 L/min sampling flow rate.

7.3 Sample Shipping

7.3.1- All field samples, trip spikes, and trip blanks will be shipped in dry ice.

7.3.2 The temperature of the samples are to be documented using an electronic temperature data logger (HOBO H8 or equivalent).

7.3.3 Samples shipped to EHLB, by an independent courier, must include the signed chain of

custody.

7.4- Samples and Sample Extracts Storage

7.4.1 All field samples must be stored in dry ice immediately after sampling.

7.4.2 Samples will be stored in the freezer immediately upon arrival from the field. The storage time limit is 14 days prior to desorption.

7.4.3 Sample extracts will be stored in the freezer immediately after desorption. All extracts must be analyzed within 14 days from extraction date.

7.4.4 Stability QC solutions are stored with each set of extracted samples.

8 Quality Control

8.1 Quality control program includes:

a) Matrix (laboratory) spikes and Trip Spikes
b) Daily liquid QC solutions
c) Storage/stability QC solutions
d) Blanks—laboratory and trip

8.2 Preparation of Stock Standard Solution

8.2.1- Attach a label to an amber 2 dram vial (8 mL). Add 7.0 ml of toluene, cap and mark the meniscus on the label with a fine tip pen. Discard about half of the solvent, cap, and weigh. The large opening on the 2 dram vial facilitates the transfer without the mitc touching the glass vial.

8.2.2- Mitc is hydrophilic therefore the following must be done quickly. Uncap the mitc bottle and quickly add approximately 50 to 80 mg of mitc into a 2 dram vial, cap, and weigh. Add solvent to the meniscus mark (to 7 mL), cap, mix and store in the refrigerator.

8.2.3 Calculate the mitc concentration in mg/mL.

8.2.4 Volumetric flask can be used with appropriate care for step 8.2.2.

8.2.5 The stock solution must be discarded after 30 days.

8.3 Preparation of Matrix Spike Solution

8.3.1 This is a standard used to spike charcoal tubes.

8.3.2 Prepare 5 ml of a High Matrix Spike Solution at a concentration of 375ng/ul in the desorbant (ethyl acetate/CS_2) from the Stock Standard Solution. Transfer to a one dram amber vial.

8.3.3 Prepare 3ml of a Low Matrix Spike Solution at a concentration of 125ng/ul by adding 1 ml of the High Matrix Spike Solution to 2 mL of the desorbant in a one dram amber vial.

8.3.4 Store both solutions in the freezer.

8.3.5 The MS Solutions should be discarded each day of use.

8.4 Preparation of Liquid Control Solutions (LC S) **[QCH and QCL]**

8.4.1 These Quality Control solutions to be used for control limits. The results are tabulated and used to generate the control chart.

8.4.2 An independent analyst prepares a mitc stock solution as per Section 8.2. The stock solution is used to prepare the QCH and QCL.

8.4.3 A High Liquid Control Solution (LCS-high) [QCH] is prepared at a concentration of 1000ng/ml.

8.4.4 A Low Liquid Control Solution (LCS-low)[QCL] is prepared at a concentration of 333ng/ml using serial dilution by taking 1 mL of the 1000 ng/mL solution and adding 2 mL of the desorbant into a 1 dram vial.

8.5 Preparation of Stability Liquid Control Spike Solutions s-QCH and s-QCL

8.5.1 These solutions are prepared at the same time as when the samples are desorbed, and stored along with the extracted samples. These control samples will show mitc degradation due to storage.

8.5.2 Prepare high and low solutions as stated in steps 8.3.2 and 8.3.3.

8.5.3 Prepare sufficient quantities as needed for the anticipated sample analysis time period and back-up sample analysis.

8.5.4 Store in autosampler vials with solid Teflon line caps along with the desorbed sample extracts. They are analyzed at the same time the samples are analyzed.

8.6 Preparation of Matrix Spikes (MS)

8.6.1 The Matrix Spikes are prepared the day before the GC analysis.

8.6.2 A Matrix Spike High at 3000ng per charcoal tube is prepared by breaking both ends of a charcoal tube, removing the back section, capping the back section, and depositing 8 ul of the High Matrix Spike Solution to the remaining front section of

charcoal using a 10 ul syringe. Cap immediately and store in a vertical position at room temperature for several hours.

8.6.3- The Matrix Spike Low at 1000 ng per charcoal tube is prepared as per step 8.6.2 using the Low Matrix Spike solution.

8.6.4 Store in freezer until analyzed.

8.7 Preparation of Trip Spikes and Lab Spikes

8.7.1 Trip Spikes and Trip Blanks sampling tubes are prepared within 24 hours of the scheduled sampling period and stored in the lab freezer prior to the scheduled pick-up. Trip Spikes and Lab Spikes are prepared at two levels each: 1000ng and 3000ng. The Trip Spikes and Tripe Blanks are transported in a dry ice container by the sampling team to the sampling location just prior to sampling. The Lab Spikes and Lab Blanks will remain in the lab freezer until they are analyzed with the field samples.

8.7.2 Open both ends of a sampling tube and cap the back end. Deposit 8ul of the High Matrix Spike Solution on to the front charcoal section and cap. Place them in a vertical position at room temperature for two hours then store in the freezer. Prepare the amount of tubes needed by the contracting agency. Half of these will be labeled "Trip Spike High", and the other half will be labeled "Lab Spike High".

8.7.3 Prepare the "Trip Spikes Low" and "Lab Spike Low" as per step 8.7.2 using 8ul of the Low Matrix Spike Solution.

8.7.4 Prepare the Trip Spikes High and Lab Spike High as per step 8.7.2 using 8ul of the High Matrix Spike Solution.

8.8 Preparation of Field Blanks and Lab Blanks

8.8.1- Open both ends of a sampling tube and cap both ends. Prepare the number required and label half as Trip Blanks and the remaining as Lab Blanks. Store in freezer until needed. The Trip Blanks must be stored under dry ice in the field along with samples.

8.8.2- All charcoal blanks must be from the same lot number.

9 Calibration and Standardization

9.1 Preparation of Calibration Standards

9.1.1- Prepare 10 ml of a 1000ng/ml standard by diluting 26.7 ul of the High Matrix Spike Solution to volume (See Section 8.3.2).

9.1.2 Prepare calibration standards at 1000, 500, 100, 50, 25, 10, 0.0 ng/ml by serial dilution.

9.1.3 The 0.0 ng/mL calibration standard is refer to as a continuing calibration verification blank (CCVB).

9.1.4 The day prior to the analysis of samples, run the standards and the QC Low and QC High (See Section 8.4). If any of the QC's is greater than +/-3 standard deviations, then corrective action must be taken.

9.1.5 Depending on the NPD stability, no daily calibration standard is used to validate a calibration curve.

9.2 Desorption Efficiency Determination (DE)

9.2.1 Desorption efficiency is determined once for each charcoal lot. Lot 120 was used for the 1999 and 2000 studies.

9.2.2 Follow the procedure used for the preparation of Matrix Spikes (9.2).

9.2.3 Spike tubes at the following levels: 0, 30, 75, 150, 300, 1500, & 3000ng. Use one tube for each level.

10 Procedure

10.3 The desorbant is ethyl acetate/CS2 (1000/1, v/v). Add 3.0ml of desorbant to a 1 dram vial and cap. Prepare the number of vials needed and label. Place in a vial rack.

10.2 Attach a small glass funnel on a ring-stand. Uncap the appropriate vial and lower the funnel so that the stem is just inside the vial and well above the desorbant. Transfer the adsorbant from the front section of the sample tube into the vial and cap immediately.

10.3 For wet samples transfer the charcoal into a small glass beaker and dry at room temperature then transfer to the charcoal to the vial as per step 10.2. The charcoal normally dries in a few hours.

10.4- Apply step 10.2 to the back section charcoal into another vial to check for break through.

10.5- Place vial rack with samples on a developing vibrator for 30 minutes.

10.6- Label 2 auto-sampler vials for each section of the charcoal tube. Ensure that the front and back sections are correctly labeled.

10.7- Shake the charcoal sample vial several times manually and let the charcoal settle. Using a glass Pasteur pipet transfer half of the sample extract into the appropriate auto-sampler vial. Transfer the remaining extract into the second vial as a backup. The backup sample vial must stored in the freezer using a solid Teflon lined cap. Mark all auto-sampler vials at the meniscus using a fine-tip pen.

10.8- Apply the above steps to all field samples and quality controls samples

10.9- Sample Analysis

10.9.1 Instrument Parameters

Carrier flow: 1.5cc/min
Hydrogen flow: 3.0cc/min
Air flow: 60cc/min
Nitrogen make-up: 10cc/min
Detector temp: 325C
Splitter mode: split-less
Injection volume: one microliter
Temperature program: 40C for 3 minutes, 5c/minute to 70c, 15c/minute to 220, no hold.

10.9.2 Analysis Sequence

10.9.2.1- A set of standards of the following concentrations:1000, 500, 100, 50, 25, 10, & 0 ng/mL are analyzed once. Standards are run from high to low.

10.9.2.2- The samples, trip spikes, lab spikes, trip blanks, and lab blanks vial are punctured twice sequentially for duplicate analyses.

10.9.2.3- The analysis sequence is as follows: first set of standards, Liquid Control Spike-low (LCS-low), 30 or less samples, Matrix Spike- low, second set of standards, Liquid Control Spike-high, 30 or less samples, Matrix Spike- high, and a third set of standards. This format is repeated for additional samples.

10.9.2.3- Field Spikes, Trip Spikes, Lab Spikes, Trip Blanks, and Lab Blanks were analyzed after the field samples.

10.9.2.5- Field Spikes, Trip Spikes, Lab Spikes, Trip Blanks, and Lab Blanks were analyzed after the field samples.

11 Calculations and Reporting

11.1 Quantitations

11.1.1 Use the data system to generate the analytical result by linear regression.
11.1.2. Verify the data system's accuracy by performing a single manual calculation on a quality control.

11.2 Reporting
11.3.1 The desorption efficiency is reported.
11.3.2 Reported values are **not** desorption efficiency corrected
11.3.3 The average of duplicate determinations and the standard deviation is reported.
11.3.4 Values below the MQL are reported as <MQL
11.3.5 The detection limit (MDL) is reported.

12 Data Assessment and Acceptance Criteria

QUALITY CONTROL DESCRIPTION	FREQUENCY	ACCEPTANCE LIMIT(S)
Calibration Blank (EHLB's Continuing Calibration Verification Blank [CCVB]): (See Section: 9.1.3)	Once each calibration curve.	Less than 4 ng/mL (MDL)
Laboratory Method Blank (EHLB's Method Blank [LMB]): (See Section: 8.7.1)	Once per Sampling episode	Less than 4 ng/mL (MDL)
Field Blank (EHLB's Field Blank [FB]): (See Section: 8.7.1)	Once per Sampling episode	Less than 4 ng/mL (MDL)
Daily Calibration Standard (Initial Calibration Verification Standard [ICVS]): (See Section: 9.1.5)	No ICVS is used. Calibration curve is generated continuously.	Not Applicable
Quality Control Standards (EHLB' Continuing Calibration Verification Standard [CCVS]): (See Section: 8.2)	At least once every 24 hours.	Results acceptable within +/- 3 standard deviation.
Field Spike (EHLB's Field Spike [FS]): (See Section: 8.6)	Once per Batch	Results acceptable within +/- 3 standard deviations.
Audit Sample [AS]: (If submitted as a sample)	Once per Sampling episode	+/- 30 percent.

13. Corrective Actions

QUALITY CONTROL DESCRIPTION	ACCEPTANCE LIMIT(S)	CORRECTIVE ACTION
Calibration Verification Blank (EHLB's Continuing Calibration Verification Blank [CCVB])	Less than 4 ng/mL (MDL)	Check desorbant , syringe rinse solvent, and gc system for contamination.

Laboratory Method Blank (EHLB's Method Blank [MB])	Less than 4 ng/mL (MDL)	Check charcoal lot for contamination, and items listed above for CCVB.
Trip Blank (EHLB's Trip Blank [TB])	Less than 4 ng/mL (MDL)	Report the results of this analysis. Determine source of contamination.
EPA's Daily Calibration Standard (Initial Calibration Verification Standard [ICVS])	Not Applicable	Not Applicable
Quality Control Standard (EHLB' Continuing Calibration Verification Standard [CCVS])	Results acceptable within +/- 3 standard deviation.	Reanalyze all samples from the quality control that passed.
Trip Spike (EHLB's Field Spike [FS])	Results acceptable within +/- 3 standard deviations.	Reanalyze trip spike. If not acceptable, report the results of this analysis. Determine the source of the problem. Report findings.
Audit Sample [AS] (If submitted as a sample)	*+/- 30 percent.*	Report the results of this analysis. Determine the source of the problem. Report findings.

14. Method Performance

Describe and document the basis for interlaboratory or EHLB generated method performance data with regard to:

14.1 Accuracy and precision: To be determined using the at least seven replicate of the lowest standard.

14.2 Accuracy and precision control limits: Within +/- 3 standard deviations.

14.3 Method Detection Limit
10.7 ng/sample ± 0. 4 ng/sample, 3 Feb 2000.

Reporting Limit
1000 ng/mL – 10 ng/mL (3000 ng/sample—30 ng/sample)

14.4 Desorption Efficiency

71.5%
3000 ng/sample—75 ng/sample
Performed 13 Jan. 2000

15. Waste Management

Dispose of all MITC related materials, including samples, standards and quality controls, by discarding into an "Organic Waste—No CS_2" labelled waste container. Send filled containers to facility storage following the Health and Safety facility protocols specified in the EHLB Health & Safety Manual.

16. References

(1) Leung, Sabrina C.: Methyl Isothiocyanate from Metham-Sodium; Determination in Air. Method No. RRC-82-35, August 26, 1982. Stauffer Chemical Corp. de Guigne Technical Center.
(2) National Environmental Laboratory Accreditation Conference. Quality Systems, Revision 6. 31 July 1997, Pg. 5-B10, "Quality Control Sample." Also, Kulasingham, G., and Lan, N., CA DHS Env. Lab Accreditation Program, personal communication.
(3) Wise, S. (stephen.wise@nist.gov), & Schantz, M. (michelle.schantz@nist.gov) NIST. Professional email reply to P. Larkin (organa@wco.com). 20 Dec 1999

17. Approvals

Prepared by: _____ Date:

Reviewed by: _____ Date:

Approved by: _____ Date: