

Determination of MITC in Air By GC/NPD or GC/TSD

1. Scope

This section method (SM) is for the analysis of MITC from air sample tubes using GC/NPD or GC/TSD and is to be followed by all authorized EMON section personnel. The reporting limit of MITC is 0.2 µg per sample by NPD and 0.05 µg per sample by TSD.

2. Principle:

Residues of MITC (methyl isothiocyanate), $\text{CH}_3\text{-N=C=S}$, that have been absorbed from the air onto activated charcoal are desorbed from the charcoal with 0.1% CS_2 in ethyl acetate. It is analyzed by gas chromatography using the nitrogen phosphorus detector or a thermionic specific detector.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 All solvents should be handled with care in a ventilated area.

4. Interferences:

No known matrix interferences that cause quantitative problems above the established reporting level were noted. However, nitrogen or phosphorus compounds with the same retention time may interfere with the quantification.

5. Apparatus and Equipment:

5.1 Test tubes, 25 mL, with Teflon lined screw cap

5.2 Assorted pipettes and micro syringes

5.3 Volumetric flasks

5.4 Files able to score the sample tubes or a Dremel (an electric rotary flex shaft tool) with $\frac{3}{4}$ " diamond saw

5.5 Thermolyne Vortex Maxi mixer

5.6 Forceps

- 5.7 HP 6890 gas chromatograph with NPD or Varian 3800 gas chromatography with TSD.
6. Reagents and Supplies
 - 6.1 Carbon disulfide, nanograde
 - 6.2 Standards:
Obtain 1.0 mg/mL reference standards of MITC from the Standard Repository, CAC, CDFA, 3292 Meadowview Road, Ca 95832.
MITC CAS Number 556-61-6
 - 6.3 Charcoal tubes: SKC #226-09 or SKC #226-16-02
 - 6.4 Ethyl Acetate, pesticide residue grade
 - 6.5 Filters, Nylon Acrodisc, 0.45 μm , Gelman Sciences
7. Standards Preparation:
 - 7.1 Dilute the 1.0 mg/mL standards, obtained from the CDFA/CAC Standards Repository, with the solution of 0.1% CS_2 in ethyl acetate. The working standards shall be prepared to cover the linear range from 0.005 $\eta\text{g}/\mu\text{L}$ to 5.0 $\eta\text{g}/\mu\text{L}$.
 - 7.2 Keep all standards in designated refrigerator or freezer for storage.
 - 7.3 The expiration date of each mixed working standard is six months from the preparation date.
8. Sample Preservation and Storage:

All samples to be extracted shall be stored in a designated freezer and all sample extracts shall be stored in a designated refrigerator ($4 \pm 3^\circ\text{C}$).
9. Test Sample Preparation:
 - 9.1 Sample Preparation
 - 9.1.1 Remove samples from freezer to the laboratory bench and allow the samples to warm to near ambient temperature.
 - 9.1.2 Fold a white sheet of 8x11 printer paper into quarters, reopen and place it under the tube to catch any spilled charcoal.

- 9.1.3 Score the tube with a file or a Dremel near the wide end of the metal spring. Break the tube by holding it with both hands at each side of the cut, with the cut pointing away from you and push the tube the the tips of your thumbs.
 - 9.1.4 For Charcoal tube SKC #226-09: Use a 9" disposable pipette to push all tube material into a test tube containing 5.0 mL of 0.1% CS₂ in ethyl acetate then cap the test tube immediately and vortex for 30 seconds.
 - 9.1.5 For Charcoal tubes SKC #226-16-02: This charcoal tube contains two segments. Use tweezers to remove the metal spring and glass-wool then place them into a test tube containing 10 mL of 0.1% CS₂ in ethyl acetate. Then, tap the side of sampling tube to allow all the charcoal in the 1st segment fall into the same test tube. Cap the test tube immediately and vortex for 20 seconds. Score and break the tube again near the 2nd segment of the tube. Use a 9" disposable pipette to push all tube material into the same test tube. Cap the test tube immediately and vortex for another 20 seconds.
 - 9.1.6 Allow samples to desorb for 30 minutes and vortex them occasionally.
 - 9.1.7 Filter the mixture through a nylon Acrodisc and collect it in two auto-sampler vials. Cap them immediately. Take one vial for GC analysis and store the one vial in a designated refrigerator for possible later use.
 - 9.2 Spike extraction: Break both ends of a charcoal tube with a file or a Dremel. Use a syringe to spike a known amount of MITC through glass wool onto the charcoal section. Follow the steps 9.1.3 through 9.1.7 to do extraction.
 - 9.3 Confirmation by mass spectrometer may be performed on GC/MSD in SIM mode (ions 73, 58, 45), if required.
- 10 Instrument Calibration:
- 10.1 The concentrations of the standards used for establishing the calibration curve were 0.005, 0.010, 0.025, 0.10, 0.25, 1.0 and 5.0 ng/μL.

10.2 A solution of 0.005 ng/ μ L correlates to the RL of 0.05 μ g/sample.

11 Analysis:

11.1 Injection Scheme

Follow the sequence of a set of calibration standards, a matrix blank, a matrix spike, a set of 12 or less test samples, a set of standards, etc.

11.2 Instrumentation and operating conditions:

11.2.1 Varian gas chromatograph model 3800 with dual injectors and dual TSD detectors. Varian auto sampler model CP8400. Varian software Galaxie version

Column: DB-FFAP, 10 m x 0.53 mm x 1.0 μ m

Gas Flow:

Carrier gas, constant flow (Helium) at 10 mL/min

He makeup flow, 25 mL/min

Hydrogen flow, 5.4 mL/min

Air flow, 190 mL/min.

Temperature:

Oven temperature program,

Rate($^{\circ}$ C/min)	Temperature ($^{\circ}$ C)	Time (minute)
Initial	45	1
15	90	4
50	220	6.6

Injector temperature: 200 $^{\circ}$ C

Detector temperature: 250 $^{\circ}$ C

Retention time: 3.0 min

Injection Volume: 2.0 μ L

11.2.2 HP 6890 gas chromatograph with dual injectors and dual NPD detectors.

Column: DB-FFAP, 10 m x 0.53 mm x 1.0 μ m

Gas Flow:

Carrier gas, constant flow (Helium) at 9 mL/min
He makeup + carrier flow, 12 mL/min
Hydrogen flow, 3.0 mL/min
Air flow, 60 mL/min.

Temperature:

Oven temperature program,
Initial temp.: 45°C for 7 minutes
Rate: 40°C/minute
Final temp.: 200°C
Injector temperature: 220 °C
Detector temperature: 250 °C

Retention time: 5.8 min
Injection Volume: 2.0 µL

11.2.3 Mass spectrometer and Operating Parameters

Model: Agilent 6890 equipped with 5972 mass selective detector
Column: RX-200 trifluoropropylmethyl polysiloxane,
60m x 0.32 mm x 1.5 µm cat #15072
Injector temperature: 210 °C
Initial column temp: 40 °C for 4 minutes
Ramp 1 rate: 12 °C per minutes
Final temperature 1: 160 °C
Ramp 2 rate: 40 °C per minutes
Final temperature 2: 240 °C for 1 minute

Mass spectrometer parameters:

Transfer line heater: 280 °C
Dwell time: 30 milliseconds
Selected ions: 72, 73, 45, 58

Injection volume: 2.0 µL
Retention time: 12.0 minutes

12. Quality Control:

- 12.1 A six point standard curve of 0.025, 0.05, 0.1, 0.5, 1.00 and 5.00 $\eta\text{g}/\mu\text{L}$ shall be obtained at the beginning and the end of each set of samples for calculating the response factors and checking the instrument performance.
- 12.2 Each set of samples shall have a matrix blank and minimum of one matrix spike sample. Each set contains up to 12 samples.
- 12.3 The matrix blank shall be free of target compounds greater or equal to the RL.
- 12.4 The recoveries of the matrix spike shall be within the control limits.
- 12.5 The retention time shall be within ± 5 seconds of that of the standard.
- 12.6 The sample must be diluted if results fall outside the linear range of the standard curve.
- 12.7 Bracketing standard response shall have a percent change less than 15%.
- 12.8 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate charcoal tubes samples are spiked with 0.10 μg or 0.15 μg of MITC solution. The standard deviation of the findings from the spiked samples are used to calculate the MDL using the follow equation:

$$\text{MDL} = tS$$

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

12.9 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client agreement, the RL is chosen in a range 1-5 times the MDL, unless otherwise agreed upon by client.

MDL data and the RL are tabulated in Appendix 1

12.10 Method Validation Recovery Data and Control Limits:

- 12.10.1 The method validation consisted of five sample sets. Each set included three levels of fortification (0.4, 3.0 and 8.0 $\mu\text{g}/\text{sample}$) and a method blank. A reagent blank shall be included when a new lot of solvent is used for extraction. All spikes, method blank and reagent blank samples were processed through the entire analytical method.
- 12.10.2 Upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average % recovery, respectively.

Method validation results and control limits are tabulated in Appendix 2

13. Calculations:

- 13.1 The quantification is based on the area counts of the target compound. The calculation is based on external standard (ESTD) and linear fit.
- 13.2 The correlation coefficient, slope, intercept of the linear regression line are calculated once the calibration standards are defined. The equation for calculating analytes is as follows:

$$y = mx + b$$

Where: y = peak response
 m = slope
 b = intercept
 x = concentration of compound

When the unit and the dilution factor are entered correctly in the analysis sequence, the software will then correctly generate the results.

- 13.3 Results can be manually calculated by a single point standard. The unit is μg per sample for all samples. This calculation is to verify the results derived from the instrument

The general equation is as follows:

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

14.1 Acceptance Criteria:

14.1.1 Peak retention time between standards, QC spikes and unknowns shall be within 5 seconds. If there is a known reason of retention time shifting, an explanation memo shall be included.

14.1.2 Peak response shall be within the calibration range.

14.1.3 The R² of calibration curve or overlay calibration curves shall be greater than 0.990.

14.1.4 Recoveries of spike QC shall be within the established control range, otherwise a rerun shall be performed.

14.1.5 The result by manual single point calculation shall agree with that by the instrument software.

14.2 Reporting:

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

14.2.2 Fill out COC, QC sheet, and control chart.

14.2.3 Prepare data package. Peer review. Report.

15 Discussion

15.1 This method is a revision of the reference 16.2. One modification was to add the Varian's Thermionic Specific Detect (TSD) to the method. The response of the TSD is more sensitive and more stable than that of the NPD.

Therefore, it allows us to improve the reporting limit from 0.2 µg/sample to 0.05 µg/sample.

- 15.2 The GC-MSD parameters have also been modified. A longer column with thicker film allows the column to retain MITC longer and to improve separation from interference peaks.

- 15.3 A storage stability study was done with this project for charcoal tube SKC226-09 and SKC 226-16-02. This study consisted of a 50ug spike level and 3 replicates over a 60 day period. These spiked samples were stored in the freezer until analyzed at 0, 1, 7, 14, 29, 46 and 60 days. Along with the storage spike samples a QC blank and QC spike were also extracted. The storage study results showed no significant degradation for the MITC within 60 days. Results for the storage study are shown in Appendix 3.

16. References:

- 16.1 ICI Americas Inc., "Methyl Isothiocyanate from Metham-Sodium Determination in Air" #RRC-35, August 26, 1982.
- 16.2 Center of Analytical Chemistry, California Department of Food and Agriculture, "MITC in Air Sample by GC/NPD" EMON#41.9, 10/28/99. A revision of 7/08/1993.

Appendix 1

The Method Detection Limit (MDL) data from NPD

	MITC Spiked (μg)	MITC Found (μg)	%
MDL-spike1	0.15	0.1314	87.6%
MDL-spike2	0.15	0.1292	86.1%
MDL-spike3	0.15	0.1245	83.0%
MDL-spike4	0.15	0.1297	86.5%
MDL-spike5	0.15	0.1191	79.4%
MDL-spike6	0.15	0.1295	86.3%
MDL-spike7	0.15	0.1211	80.7%
Average		0.1264	84.2%
STDEV		0.0048	3.20%
MDL=3.143xSTDEV		0.0151	
RL*		0.20	

*Due to NPD response consistency problem, we set the RL at larger than 5 X of its MDL

The Method Detection Limit (MDL) data from TSD

	MITC Spiked (μg)	MITC Found by Detector 1 (μg)	MITC Found by Detector 2 (μg)
MDL-spike1	0.10	0.1085	0.0930
MDL-spike2	0.10	0.1100	0.0915
MDL-spike3	0.10	0.1190	0.1010
MDL-spike4	0.10	0.1210	0.1010
MDL-spike5	0.10	0.1200	0.1015
MDL-spike6	0.10	0.1165	0.1000
MDL-spike7	0.10	0.1155	0.1000
Average		0.1155	0.0983
STDEV		0.0049	0.0042
MDL=3.143xSTDEV		0.015	0.013
RL		0.05	0.05

Appendix 1 *continued*

The Method Detection Limit (MDL) data MITC in SKC 226-16-02 charcoal tube from TSD

	MITC Spiked (µg)	MITC Found (µg)	%
MDL-spike1	0.15	0.0865	87.6%
MDL-spike2	0.15	0.0850	85.0%
MDL-spike3	0.15	0.0843	84.3%
MDL-spike4	0.15	0.0845	84.5%
MDL-spike5	0.15	0.0820	82.0%
MDL-spike6	0.15	0.0901	90.1%
MDL-spike7	0.15	0.0780	78.0%
Average		0.0843	84.3%
STDEV		0.00374	
MDL=3.143xSTDEV		0.01176	
RL*		0.05	

Appendix 2

Method Validation Data for MITC from NPD

Spike Level	Set1	Set 2	Set 3	Set 4	Set 5
MITC Spiked (µg)	MITC found (%)	MITC found (%)	MITC found (%)	MITC found (%)	MITC found (%)
0.4	83.8	91.2	89.0	104.3	86.4
3.0	82.4	88.4	96.0	102.8	87.9
8.0	84.7	85.7	77.0	80.8	80.6

Average 88.07%
 Standard Deviation 7.82%
 Upper Control Limit 111.52%
 Lower Control Limit 64.61%

Appendix 2 *continued*

Method Validation Data for MITC in SKC 226-09 charcoal tube from TSD

Spike Level	Set1	Set 2	Set 3	Set 4	Set 5
MITC Spiked (µg)	MITC found (%)	MITC found (%)	MITC found (%)	MITC found (%)	MITC found (%)
0.1	102	99.0	96.0	99.0	97.0
0.4	82.5	87.5	87.5	90.0	85.0
3.0	97.3	106.7	103.3	93.0	112.7
8.0	97.8	98.5	92.3	86.9	100.3

Average 95.72%
Standard Deviation 7.67%
Upper Control Limit 118.73%
Lower Control Limit 72.69%

Method Validation Data for MITC in SKC 226-16-02 charcoal tube from TSD

Spike Level	Set 1	Set 2	Set 3
MITC Spiked (µg)	Recovery (%)	Recovery (%)	Recovery (%)
1.0	81.2	81.1	78.3
10.0	76.7	78.2	78.8
100.0	77.8	73.7	78.8

Spike Level	Set 4	Set 5	Set 6
MITC Spiked (µg)	Recovery (%)	Recovery (%)	Recovery (%)
0.5	71.8	75.4	72.2
1.0	68.2	73.3	74.5
10.0	64.8	72.1	72.9

Average 74.99%
Standard Deviation 4.36%
Upper Control Limit 88.06%
Lower Control Limit 61.92%

Appendix 3

The Storage Stability Study Results

% Recoveries

Tube size	Samples	Day 0 1/22/07	Day 1 1/23/07	Day 7 1/29/07	Day 14 2/5/08	Day 29 2/20/07	Day 46 3/9/08	Day 60 3/23/09
Small	QC Blank	ND	ND	ND	ND	ND	ND	ND
SKC226-09	QC Spike	88.7%	96.7%	86.0%	91.3%	91.0%	91.3%	81.7%
	Spike 1	84.4%	83.0%	78.4%	78.6%	78.4%	79.2%	74.2%
	Spike 2	81.8%	82.6%	79.4%	75.4%	77.0%	78.0%	74.2%
	Spike 3	84.4%	78.6%	80.6%	77.4%	76.2%	81.0%	73.6%
Large	QC Blank	ND	ND	ND	ND	ND	ND	ND
SKC 226-16-02	QC Spike	79.7%	85.3%	81.7%	79.7%	84.0%	77.7%	73.3%
	Spike 1	74.2%	69.0%	72.0%	70.2%	70.4%	70.2%	67.2%
	Spike 2	70.8%	68.8%	73.8%	68.6%	68.8%	69.8%	66.0%
	Spike 3	71.6%	70.0%	71.2%	68.2%	68.4%	68.4%	67.4%

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