

Determination of MITC in Air by GC-MS

1. Scope

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

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 1.0% CS_2 in ethyl acetate. It is analyzed by GC-MS.

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.

Apparatus and Equipment:

- 4.1 Test tubes, 25 mL, with Teflon lined screw cap
- 4.2 Assorted pipettes and micro syringes
- 4.3 Volumetric flasks
- 4.4 Files able to score the sample tubes or a Dremel (an electric rotary flex shaft tool) with $\frac{3}{4}$ " diamond saw
- 4.5 Thermolyne Vortex Maxi mixer
- 4.6 Forceps
- 4.7 Agilent Technologies gas chromatograph GC (7890A) with Agilent Technologies mass detector MSD (5975C inert XL).

5. Reagents and Supplies

- 5.1 Carbon disulfide, Nano grade
- 5.2 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
- 5.3 Charcoal tubes: SKC #226-16-02 or SKC #226-09
- 5.4 Ethyl Acetate, pesticide residue grade
- 5.5 Filters, Nylon Acrodisc, 0.45 μm , Gelman Sciences

6. Standards Preparation:

- 6.1 Dilute the 1.0 mg/mL standards, obtained from the CDFA/CAC Standards Repository, with the solution of 1.0% 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 1.0 $\eta\text{g}/\mu\text{L}$.
- 6.2 Keep all standards in designated refrigerator or freezer for storage.
- 6.3 The expiration date of each mixed working standard is six months from the preparation date.

7. 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 ($4 \pm 3^\circ\text{C}$).

8. Test Sample Preparation:

- 8.1 Sample Preparation
 - 8.1.1 Remove samples from freezer to the laboratory bench and allow the samples to warm to near ambient temperature.
 - 8.1.2 Fold a white sheet of 8x11 printer paper into quarters, reopen and place it under the tube to catch any spilled charcoal.
 - 8.1.3 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 tips with your thumbs.

- 8.1.4 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 1.0% CS₂ in ethyl acetate then cap the test tube immediately and vortex for 30 seconds.

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 1.0% 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. Use a 9" disposable pipette to push the 2nd segment tube material into the same test tube. Cap the test tube immediately and vortex for 60 seconds.

- 8.1.5 Allow samples to desorb for 30 minutes and vortex them for 60 seconds.

- 8.1.6 Filter the mixture through a nylon Acrodisc and collect it in two auto-sampler vials. Cap them immediately. Take one vial for GC-MS analysis and store the one vial in a designated refrigerator for possible later use.

- 8.2 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 Instrument Calibration:

- 9.1 The concentrations of the standards used for establishing the calibration curve were 0.005, 0.010, 0.025, 0.10, 0.25, and 1.0 ng/μL.

- 9.2 A solution of 0.005 ng/μL correlates to the RL of 0.05 μg/sample.

10 Analysis:

10.1 Injection Scheme

Follow the sequence of a set of calibration standards, a matrix blank, a matrix spike, a set of 20 or less test samples, a set of standards, etc.

10.2 Instrumentation and operating conditions:

10.2.1 Agilent Technologies gas chromatograph model 7890B with Agilent Technologies mass detectors model 5977B MSD

Column: HP-FFAP, 25 m x 0.320 mm x 0.50 μ m

Gas Flow:

Carrier gas, constant pressure (Helium) at 5 psi

Temperature:

Oven temperature program,		Temperature ($^{\circ}$ C)	Time (minute)
Rate ($^{\circ}$ C/min)			
Initial	60	4	
22	160	4	
25	220	8	

Injector temperature: 230 $^{\circ}$ C

Retention time: 5.34 min

Injection Volume: 2.0 μ L

Mass spectrometer parameters:

Transfer line heater: 230 $^{\circ}$ C
Dwell time: 50 milliseconds
Selected ions: 72, 73

11. Quality Control:

- 11.1 A six-point standard curve of 0.1, 0.015, 0.025, 0.50, 1.0, 2.5 and 6.µg/mL shall be obtained at the beginning and the end of each set of samples for calculating the response factors and checking the instrument performance.
- 11.2 Each set of samples shall have a matrix blank and minimum of one matrix spike sample. Each set contains up to 20 samples.
- 11.3 The matrix blank shall be free of target compounds greater or equal to the RL.
- 11.4 The recoveries of the matrix spike shall be within the control limits.
- 11.5 The retention time shall be within ± 5 seconds of that of the standard.
- 11.6 The sample must be diluted if results fall outside the linear range of the standard curve.
- 11.7 Bracketing standard response shall have a percent change less than 20%.
- 11.8 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 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.

- 11.9 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

11.10 Method Validation Recovery Data and Control Limits:

- 11.10.1 The method validation consisted of five sample sets. Each set included five levels of fortification (0.1 0.2 0.5 0.7 and 1.0 µg/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.
- 11.10.2 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

12. Calculations:

- 12.1 The quantification is based on the area counts of the target compound. The calculation is based on external standard (ESTD) and linear fit.
- 12.2 The correlation coefficient, slope and 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.

- 12.3 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:

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

13 Acceptance Criteria:

13.1 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.

13.2 Peak response shall be within the calibration range.

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

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

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

13.6 Reporting:

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

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

13.6.3 Prepare data package. Peer review. Report.

14 Discussion

- 14.1 This method is a revision of the reference 41.9. One modification was to add GC-MS analysis
- 14.2 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.
- 14.3 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.

15. References:

- 15.1 ICI Americas Inc., "Methyl Isothiocyanate from Metham-Sodium Determination in Air" #RRC-35, August 26, 1982.
- 15.2 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 MITC in SKC 226-16-02 charcoal tube The Method Detection Limit (MDL) data from GC-MS

	MITC Spiked (µg)	MITC Found (µg)	%
MDL-spike1	0.10	0.0697	69.7%
MDL-spike2	0.10	0.0669	66.9%
MDL-spike3	0.10	0.0542	54.2%
MDL-spike4	0.10	0.0603	60.3%
MDL-spike5	0.10	0.0607	60.7%
MDL-spike6	0.10	0.0537	53.7%
MDL-spike7	0.10	0.0651	65.1%
Average		0.0615	61.5%
STDEV		0.0061	
MDL=3.143xSTDEV		0.0192	
RL*		0.05	

Appendix 2

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

Spike Level MITC Spike (µg)	Set1 MITC found (%)	Set2 MITC found (%)	Set3 MITC found (%)
0.10	99.7	86.4	97.7
0.15	94.0	91.5	98.6
0.25	77.2	93.3	89.1
0.50	86.4	84.3	83.0
1.0	90.7	87.2	88.9
2.5	87.1	89.8	88.3
6.5	90.0	93.7	90.2

Average: 89.9%
Standard Deviation 5.30%
UCL 106%
LCL 74.0%

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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Revision Log:

Date	What was revised? Why?
9/20/04	Formatting to ISO format
9/20/04	Adding a new instrument (Varian TSD) and the parameters to the method
9/20/04	Reducing reporting limit to 0.05 µg from 0.2 µg
9/20/04	Adding new validation data obtained from TSD to the method
9/20/04	Modifying the confirmation MSD method parameters
6/08/11	Adding the extraction procedure and validation data for analysis of MITC in the SKC 226-16-02 charcoal tube
1/11/18	Adding new MDL and validation data obtained from GC-MS to the method
3/15/18	Changed CS2 concentration in principle section and section 7.1
	Changed CS2 concentration and vortex time in sections 9.1.4 and 9.1.5
	Removed section 9.3 about MSD confirmation.
	Added new validation results to appendix
	Changed EPM 1 signature name