Quality Assurance Project Plan
for
Monitoring of Seasonal Concentrations of Methyl Isothiocyanate (MITC) in Ambient Air in Communities of High-Use Regions

Fiscal year 2016/2017

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## Table of Contents

List of Figures .................................................................................................................. 3  
List of Tables ................................................................................................................... 3  

1 **Project Management Elements** .............................................................................. 4  
1.1 Distribution List ........................................................................................................ 4  
1.2 Study Organization .................................................................................................... 5  
1.2.1 Table of Responsibilities ...................................................................................... 5  
1.3 Study Definition/Background ................................................................................... 6  
1.4 Study Description ...................................................................................................... 6  
1.5 Quality Objectives and Criteria for Measurement Data ........................................... 14  
1.5.1 Field Sampling Quality Control .......................................................................... 14  
1.5.2 Quality Assurance ............................................................................................... 15  
1.6 Training ...................................................................................................................... 15  
1.6.1 Training Requirements ......................................................................................... 15  
1.7 Documents and Records ............................................................................................ 16  
1.7.1 List of Forms and Filing Procedures for Paper Files and Records ...................... 16  
1.7.2 Electronic Record Keeping—Forms .................................................................... 16  

2 **Data Generation and Acquisition** ........................................................................... 16  
2.1 Sampling Design ...................................................................................................... 16  
2.2 Sampling Methods ................................................................................................... 17  
2.2.1 Sample Collection ............................................................................................... 17  
2.2.2 Equipment Decontamination ............................................................................ 17  
2.3 Sample Handling and Custody Requirements ......................................................... 17  
2.3.1 Sample Custody, Sample Shipping, Chain of Custody Procedures .................. 18  
2.3.1.1 Shipping Procedures ...................................................................................... 18  
2.4 Analytical Methods ................................................................................................. 18  
2.5 Quality Control ........................................................................................................ 19  
2.6 Instrument/Equipment Testing, Inspection, and Maintenance ............................... 19  
2.7 Instrument/Equipment Calibration and Frequency ................................................... 19  
2.8 Inspection/Acceptance of Supplies and Consumables ............................................ 19  
2.9 Non-direct Measurements ....................................................................................... 19  
2.10 Data Management—Electronic Record Keeping ..................................................... 20  

3 **Assessment and Oversight** ...................................................................................... 20  
3.1 Assessment and Response Actions .......................................................................... 20  
3.2 Reports to Management ............................................................................................ 21  

4 **Data Validation and Usability** .................................................................................. 21  
4.1 Data Review, Validation, and Verification ................................................................ 21  
4.2 Verification and Validation Methods ........................................................................ 21  
4.3 Reconciliation with User Requirements ..................................................................... 21  

5 **References** .............................................................................................................. 22  

6 **Appendices** ............................................................................................................ 24
List of Figures

Figure 1. Reported use of MITC (pounds of a.i.) by month during 2012 – 2014 for the top five California counties...............................................................................................................................................7

Figure 2. Reported use of MITC-generators (pounds of a.i.) applied by township (6x6 miles) in California for 2012 – 2014. ..................................................................................................................................8

Figure 3. Reported use of MITC-generators (pounds of a.i.) applied by section (1x1 miles) in Kern and Santa Barbara Counties for 2012 – 2014. .................................................................................................10

Figure 4. Wind roses for selected CIMIS stations in Kern and Santa Barbara Counties for the period between January 1, 2011 and December 31, 2015. .................................................................11

List of Tables

Table 1. Distribution list................................................................................................................................4

Table 2. Table of Responsibilities...............................................................................................................5

Table 3. Top 5 California counties with highest reported MITC-generators use (pounds a.i.) from 2012 – 2014..................................................................................................................................................7

Table 4. Rankings of California’s top-10 communities based upon averaging of regional, local, and community “zone” MITC-generators use for 2012 – 2014...............................................................9

Table 5. Proposed scheduled sampling dates for monitoring. .................................................................13

Table 6. Summary of Holding Times and Storage Temperatures. .............................................................15
1 Project Management Elements

1.1 Distribution List

The following individuals will receive copies of the approved Quality Assurance Project Plan (QAPP) and any subsequent revisions.

Table 1. Distribution list.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>Organization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabiola Estrada</td>
<td>Project Officer, Land Division</td>
<td>US EPA</td>
</tr>
<tr>
<td>Eugenia McNaughton</td>
<td>Manager, Quality Assurance Section</td>
<td>US EPA</td>
</tr>
<tr>
<td>Pam Wofford</td>
<td>Acting Branch Chief, Environmental Program Manager</td>
<td>EMON, DPR</td>
</tr>
<tr>
<td>Edgar Vidrio</td>
<td>Senior Environmental Scientist (Supervisor)</td>
<td>EMON, DPR</td>
</tr>
<tr>
<td>Sue Peoples</td>
<td>Senior Environmental Scientist (Specialist)</td>
<td>EMON, DPR</td>
</tr>
<tr>
<td>Elaine Wong</td>
<td>Environmental Program Manager</td>
<td>Center for Analytical Chemistry, CDFA</td>
</tr>
<tr>
<td>Christopher Collins</td>
<td>Environmental Scientist</td>
<td>EMON, DPR</td>
</tr>
</tbody>
</table>
1.2 Study Organization

1.2.1 Table of Responsibilities

Table 2. Table of Responsibilities.

<table>
<thead>
<tr>
<th>Title</th>
<th>Responsibilities</th>
<th>Name</th>
<th>Phone No. and Email</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental Program Manager, Acting Branch Chief</td>
<td>Air Program Manager</td>
<td>Pam Wofford</td>
<td>(916) 324-4297  <a href="mailto:Pam.Wofford@cdpr.ca.gov">Pam.Wofford@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Senior Environmental Scientist (Supervisor)</td>
<td>Supervises the study</td>
<td>Edgar Vidrio</td>
<td>(916) 323-2778  <a href="mailto:Edgar.Vidrio@cdpr.ca.gov">Edgar.Vidrio@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Environmental Program Manager</td>
<td>Ensures that laboratory services meet all internal and project-specific QA/QC requirements</td>
<td>Elaine Wong, Center for Analytical Chemistry, CDFA</td>
<td>(916) 262-1529  <a href="mailto:Elaine.Wong@cdpr.ca.gov">Elaine.Wong@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Senior Environmental Scientist (Specialist)</td>
<td>Laboratory liaison between CDFA and EMON</td>
<td>Sue Peoples</td>
<td>(916) 322-3082  <a href="mailto:Sue.Peoples@cdpr.ca.gov">Sue.Peoples@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Environmental Scientist</td>
<td>Study Lead</td>
<td>Christopher Collins</td>
<td>(916) 324-4124  <a href="mailto:Christopher.Collins@cdpr.ca.gov">Christopher.Collins@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Environmental Scientist</td>
<td>Study Field Coordinator</td>
<td>Kelly Heal</td>
<td>(916) 445-0113  <a href="mailto:Kelly.Heal@cdpr.ca.gov">Kelly.Heal@cdpr.ca.gov</a></td>
</tr>
<tr>
<td>Environmental Scientist</td>
<td>Sampling Personnel</td>
<td>Clarice Ando</td>
<td>(559) 297-5406  <a href="mailto:Clarice.Ando@cdpr.ca.gov">Clarice.Ando@cdpr.ca.gov</a></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Colin Brown</td>
<td>(916) 445-9579  <a href="mailto:Colin.Brown@cdpr.ca.gov">Colin.Brown@cdpr.ca.gov</a></td>
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<tr>
<td></td>
<td></td>
<td>Amy Budahn</td>
<td>(916) 324-4086  <a href="mailto:Amy.Budahn@cdpr.ca.gov">Amy.Budahn@cdpr.ca.gov</a></td>
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<tr>
<td></td>
<td></td>
<td>Kelsey Craig</td>
<td>(916) 324-4096  <a href="mailto:Kelsey.Craig@cdpr.ca.gov">Kelsey.Craig@cdpr.ca.gov</a></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jazmin Gonzalez</td>
<td>(916) 445-7227  <a href="mailto:Jazmin.Gonzalez@cdpr.ca.gov">Jazmin.Gonzalez@cdpr.ca.gov</a></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kenneth King</td>
<td>(916) 445-3677  <a href="mailto:Kenneth.D.King@cdpr.ca.gov">Kenneth.D.King@cdpr.ca.gov</a></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fabio Sartori</td>
<td>(916) 327-7479  <a href="mailto:Fabio.Sartori@cdpr.ca.gov">Fabio.Sartori@cdpr.ca.gov</a></td>
</tr>
</tbody>
</table>
### 1.3 Study Definition/Background

Methyl isothiocyanate (MITC) is a pesticide widely used throughout the state of California with over 11 million pounds of active ingredient applied in 2014 alone. It is a highly volatile compound with broad, non-selective biocidal activity, which results from the breakdown of metam sodium, metam potassium, or dazomet in the environment (hereafter referred to as MITC-generators), particularly when in the presence of water (US EPA 2008). Exposure to MITC can cause sensory irritation in the eye and nose. In California, Kern and Fresno Counties have had the greatest use of MITC from 2012 through 2014, the most recent years for which data are available (see Table 3).

From 1993 – 2002, either the California Department of Pesticide Regulation (DPR) or the California Air Resources Board (ARB), at DPR’s request, have conducted application-site air monitoring for MITC in various counties to estimate acute exposures. Those results showed significant levels of MITC (880 µg/m³) were detected at up to 60 feet from an MITC soil fumigation and 2,450 ppb (12,681 µg/m³) at 5 meters (16.4 feet) from a fixed-set sprinkler MITC application (ARB 1994, Wofford et al. 1994). From 1993 to 2002, DPR conducted several seasonal ambient air monitoring studies for MITC in Contra Costa, Kern and Santa Barbara Counties. DPR has since set acute health screening levels for MITC at 66,000 ng/m³ (66 µg/m³), subchronic screening levels at 3,000 ng/m³ and chronic screening levels at 300 ng/m³ (DPR 2011).

In 2011, as part of DPR’s mandate for “continuous evaluation” of currently registered pesticides, DPR began conducting ambient air monitoring for multiple pesticides, including MITC, as part of its Air Monitoring Network (AMN) (DPR 2011) to estimate subchronic and chronic exposures to the pesticides monitored. To place the monitoring results in a health-based context, DPR developed health screening levels for all pesticides included in the AMN, including MITC, which are listed above (DPR 2011). As part of this long-term monitoring study, a weekly 24-hour air sample is collected in several communities (including one in Kern County) and analyzed for multiple pesticides. The AMN sampling locations were selected based on high-use and toxicity of multiple pesticides, which may not necessarily include the areas with the greatest MITC use. To estimate current seasonal exposures to MITC, DPR proposes to conduct seasonal ambient air monitoring for MITC in multiple communities located in Kern and Santa Barbara Counties during the high-use period, beginning June 1st and ending August 31st (approximately 12 weeks). The goals of this study are to:

- Assist in evaluating seasonal (subchronic) MITC exposure for bystanders near areas of highest MITC use,
- Evaluate the effectiveness of current regulations and mitigation efforts, and
- Complement ongoing seasonal and long-term MITC monitoring efforts by DPR and ARB in other parts of the state.

### 1.4 Study Description

DPR’s Pesticide Use Report (PUR) database contains a comprehensive statewide record of pesticide applications in California. Applicators are required to submit records of all pesticide applications to DPR. The submitted PUR contains information on the pesticide product used, crop type, application date, application amount, application type, and the application location. The PUR database provides location information as a one-mile square section defined by the Public Land Survey System (PLSS). DPR staff queried the PUR database to obtain MITC use data for the calendar years 2012 – 2014. For the purposes of this document, MITC use data refers to the aggregate sum of the MITC-generators metam sodium,
metam potassium, and dazomet for the calendars years 2012 - 2014. Table 3 shows reported MITC use during this timeframe for the top 5 California counties with the highest use. Kern County, located in the southern part of the San Joaquin Valley, had the highest reported MITC use for all years queried.

The application of MITC-generators occurs seasonally and depends upon the commodity grown. The amounts applied vary by both the time of year and region. Figure 1 charts the distribution, by month, of the total use of MITC-generators for 2012 – 2014 in the top 5 use counties. Figure 2 displays the cumulative use of MITC-generators (pounds of active ingredient, a.i.) at the township level in California for 2012 – 2014.

**Table 3.** Top 5 California counties with highest reported MITC-generators use (pounds a.i.) from 2012 – 2014.

<table>
<thead>
<tr>
<th>County</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kern</td>
<td>4,259,582</td>
<td>5,220,262</td>
<td>3,595,769</td>
<td>13,075,613</td>
</tr>
<tr>
<td>Fresno</td>
<td>3,926,102</td>
<td>3,502,192</td>
<td>2,664,859</td>
<td>10,093,153</td>
</tr>
<tr>
<td>Merced</td>
<td>754,407</td>
<td>914,739</td>
<td>1,344,758</td>
<td>3,013,904</td>
</tr>
<tr>
<td>Kings</td>
<td>716,347</td>
<td>736,931</td>
<td>718,296</td>
<td>2,171,573</td>
</tr>
<tr>
<td>Ventura</td>
<td>1,078,230</td>
<td>453,255</td>
<td>349,024</td>
<td>1,880,508</td>
</tr>
</tbody>
</table>

**Figure 1.** Reported use of MITC (pounds of a.i.) by month during 2012 – 2014 for the top 5 California counties.
Figure 2. Reported use of MITC-generators (pounds of a.i.) applied by township (6x6 miles) in California for 2012 – 2014.
DPR reviewed all MITC-generator use reports submitted to DPR for applications made between 2012 and 2014 in order to identify communities near areas of highest use. The list of communities includes all cities and census-designated places (CDPs) located within California as described by the 2010 United States Census, with the exception of communities within the urban counties of Los Angeles, Orange, San Diego, and San Francisco, where there is not much reported agricultural use.

Three non-overlapping spatial categories (or ‘zones’) were used to rank the level of MITC-generator use surrounding each community:

- Community zone: use falling within the community boundary,
- Local zone: use between 0-1 mile out from the community boundary, and
- Regional zone: use between 1-5 miles out from the community boundary.

Multiple queries of the PUR database provided MITC-generator use data for every “zone” with a record of use from 2012-2014. In cases where a PLSS section was only partially included within the zone boundary, the use of that section was added to the total use in that zone in proportion to the area of the section falling within the zone. Communities were ranked independently for MITC-generator use within the three zones and a final statewide ranking was assigned based on the average use of the three zones. Table 4 shows the top 10 California communities based on average MITC-generator use of the three zones from 2012-2014. Seven out of the top 10 California highest-use communities are located in either Kern County or Santa Barbara County; these communities are displayed in Table 4 as shaded rows. Figure 4 shows the cumulative use of MITC-generators (pounds of active ingredient, a.i.) at the one square mile section level in Kern County and the east section of Santa Barbara County for 2012 – 2014.

**Table 4.** Ranking of California’s top 10 communities based upon averaging of regional, local, and community “zone” MITC-generator use for 2012 – 2014.

<table>
<thead>
<tr>
<th>Statewide Community Ranking</th>
<th>Community Name</th>
<th>County</th>
<th>Average MITC-Generator Use (lbs)</th>
<th>Average “Zone” Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mettler CDP</td>
<td>Kern</td>
<td>33,940</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>Cuyama CDP</td>
<td>Santa Barbara</td>
<td>25,615</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Edmundson Acres CDP</td>
<td>Kern</td>
<td>22,112</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>New Cuyama CDP</td>
<td>Santa Barbara</td>
<td>18,890</td>
<td>4.3</td>
</tr>
<tr>
<td>5</td>
<td>El Rio CDP</td>
<td>Ventura</td>
<td>14,405</td>
<td>9.7</td>
</tr>
<tr>
<td>6</td>
<td>Weedpatch CDP</td>
<td>Kern</td>
<td>9,837</td>
<td>7.3</td>
</tr>
<tr>
<td>7</td>
<td>Huron city</td>
<td>Fresno</td>
<td>7,993</td>
<td>9.7</td>
</tr>
<tr>
<td>8</td>
<td>Rosedale CDP</td>
<td>Kern</td>
<td>7,544</td>
<td>15.0</td>
</tr>
<tr>
<td>9</td>
<td>Arvin city</td>
<td>Kern</td>
<td>6,977</td>
<td>12.3</td>
</tr>
<tr>
<td>10</td>
<td>Cantua Creek CDP</td>
<td>Fresno</td>
<td>5,741</td>
<td>16.0</td>
</tr>
</tbody>
</table>

CDP: Census-designated place as defined by the United States Census Bureau.
Figure 3. Reported use of MITC-generators (pounds of a.i.) applied by section (1x1 miles) in Kern and Santa Barbara Counties for 2012 – 2014.

When multiple sampling site locations within a selected high-use ranking community are available to DPR for study inclusion, DPR plans to use weather patterns to prioritize the site locations that are downwind of high-use areas as these locations have the potential to lead to the higher exposure levels. Meteorological data has been obtained from the California Irrigation Management Information System (CIMIS), a network of automated weather monitoring stations managed by the California Department of Water Resources. These data include wind direction and wind speed measurements collected 2 meters above ground height. Weather data was downloaded in hourly format for the period between January 1, 2011, and December 31, 2015. Data was then aggregated and summarized as a wind rose, a graphical tool that provides a visual summary of the distribution of wind direction and speed at a monitoring location. The spokes on a wind rose indicate the strength and frequency with which a wind blows from a particular direction. The free WRPLOT View tool from Lakes Environmental Software was used to develop wind roses for each 5-year period. Figure 4 displays all wind roses for selected active CIMIS stations in Kern and Santa Barbara counties for the period between January 1, 2011, and December 31, 2015.
Figure 4. Wind roses for selected CIMIS stations in Kern and Santa Barbara Counties for the period between January 1, 2011, and December 31, 2015.

In order to assess current seasonal exposures to MITC in the region that ranks the highest for MITC-generator use in California, DPR proposes to conduct ambient air monitoring for MITC in Kern and Santa Barbara Counties. A total of five sampling sites in Kern and Santa Barbara County communities will be selected for monitoring; four sampling sites will be selected from the high-use communities listed in Table 4 and one additional site will be placed in a community with lower pesticide use to serve as a background comparison site. To obtain a representative region’s seasonal ambient MITC concentrations, one sampling site per community will be selected. No sampling site locations will be farther than 1-2 miles from MITC-generator use as reported on DPR’s PUR Database, with the exception of the
Selection of the sampling site location will follow the prioritization scheme listed below:

1. Preference will be given to communities with the highest overall use rankings as listed in Table 4.
2. DPR staff will locate all feasible sampling site locations within the high-use ranking community.
   a. Preference will be given to public buildings (schools, police stations, city halls, etc.) or to locations that are currently being used for air monitoring by DPR or by the California Air Resources Board.
3. For each possible sampling site location, the following site feasibility questions are methodically assessed:
   a. Does the location meet the U.S. EPA ambient air siting requirements (40 CFR Part 58; listed on Section 2.1 of this document)?
   b. Is the site secure to both equipment and sampling personnel and does it have onsite electrical available?
   c. Does the owner/operator of the potential sampling site grant DPR staff permission to conduct ambient air monitoring on their property during the duration of the study?
   d. Is there more than one available sampling site location in the community to choose from that have satisfied the above requirements?
      i. If more than one site is available, weather patterns are then used to prioritize the monitoring site locations that are downwind of high use areas
   e. If the answer to any of the above questions is negative, then that site is eliminated from study inclusion consideration and another possible sampling location within the community is evaluated or we move on to next highest ranking community if all possible sampling locations have been exhausted.

Once all five sampling site locations are selected for monitoring, ambient air monitoring will be conducted over a 12-week period corresponding to the period of high use of MITC-generators in the area. At each sampling site, four consecutive 24-hour samples will be collected each week of the 12-week sampling period. The four-day sampling period will begin each week on a chosen day over the full seven-day week, including weekends, such that sampling dates are evenly distributed (Table 5). In addition to the primary samples, quality control samples including co-located duplicates, fortified field spikes, and trip blank samples will be collected at a rate of 10% of primary samples collected during the 12–week sampling period. Field spike and co-located duplicate samples will be collected under the same environmental (e.g., temperature, humidity, exposure to sunlight) and monitoring conditions (e.g., air flow rates, sample transportation and storage) as the primary samples. Back-up samples to evaluate for breakthrough in the field samples will also be collected as detailed in Section 1.5.2. One sampling site location, excluding the background site, will be utilized for the collection of all quality control samples for this study in addition to collecting primary samples.

In the case of dangerous adverse weather conditions (i.e., electrical thunderstorms, driving visibility issues, etc.), sampling equipment problems, sampling issues, or sampling personnel needs, sampling can be extended for another day or two in order to collect any lost samples for that week, if there are any days available before the next scheduled sampling date. Deviations from the sampling schedule proposed on Table 5 will need to be discussed with and agreed upon by the Air Program Supervisor and the Study Leader.
Table 5. Proposed sampling schedule and number of samples to be collected for study.

<table>
<thead>
<tr>
<th>Proposed Sampling Schedule</th>
<th>Number of Primary Samples</th>
<th>Quality Control Samples</th>
<th>Back-up Samples</th>
<th>Total Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunday</td>
<td>Monday</td>
<td>Tuesday</td>
<td>Wednesday</td>
<td>Thursday</td>
</tr>
<tr>
<td>Week 1</td>
<td>X²</td>
<td>X³</td>
<td>X</td>
<td>X⁴</td>
</tr>
<tr>
<td>Week 2</td>
<td>X⁴</td>
<td>X³</td>
<td>X⁵</td>
<td>X</td>
</tr>
<tr>
<td>Week 3</td>
<td>X³</td>
<td>X⁵</td>
<td>X</td>
<td>X⁴</td>
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<tr>
<td>Week 4</td>
<td>X³</td>
<td>X⁵</td>
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<td>Week 5</td>
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<tr>
<td>Week 12</td>
<td>X³</td>
<td>X⁵</td>
<td>X⁴</td>
<td>X⁵</td>
</tr>
</tbody>
</table>

1. Sampling to begin Monday, June 5th.
2. Indicates collection of spiked sample.
3. Indicates collection of co-located duplicate sample.
4. Indicates collection of trip blank.
5. Indicates collection of back-up sample on a primary sample.
6. Indicates collection of back-up sample on a spiked sample.
Collected air samples will be analyzed by California’s Department of Food and Agriculture’s (CDFA) Center for Analytical Chemistry (3292 Meadowview Rd, Sacramento, CA 95832) for residues of MITC as described by Lee (2004). MITC extraction from the sorbent medium involves using carbon disulfide in ethyl acetate with subsequent analysis using gas chromatography (GC) with a nitrogen/phosphorous detector. Analysis of the samples will quantify the amount of captured MITC which will then be used to determine the concentration of MITC present in ambient air at the selected locations during the time of sampling. These results can then be compared to the acute (66,000 ng/m³) and sub-chronic (3,000 ng/m³) human health screening levels for MITC as determined by DPR (DPR 2011).

1.5  **Quality Objectives and Criteria for Measurement Data**

1.5.1  Field Sampling Quality Control

Four types of quality control samples will be systematically assigned for collection in the field over the course of the ambient air monitoring study:

1. Trip blanks, defined as new, clean sorbent tubes that have not been exposed to air prior to sampling. Upon collection of field samples from the site, the sorbent tube is exposed to the air momentarily and then treated as a collected field sample. Their purpose is to periodically assess possible contamination due to field sample handling or laboratory handling techniques.

2. Fortified field spikes are sorbent tubes that have a known quantity of MITC applied by the analytical laboratory prior to being taken to the field. In the field, fortified field spikes are then attached to sampling pumps and operated under identical conditions and time periods as primary samples. The comparison of the measured MITC concentration to the known quantity added will determine the recovery rate and provide information on any change in the ability to recover MITC under field conditions. If fortified field spike MITC recoveries fall outside the recovery limit, a reassessment of the field and laboratory procedures will be conducted. Laboratory staff will investigate the cause of the low recoveries and implement corrective action as required. Field sample data will be evaluated for potential impact, and flagged as appropriate.

3. Co-located duplicate samples are collected directly adjacent to primary samples under the same conditions and time period. Recovery of MITC between the primary samples and co-located duplicates are compared to evaluate laboratory analytical instrument precision. Compared samples with a variation greater than 50% in recovery will result in reassessment of the field and laboratory procedures. Should this occur, laboratory staff would follow similar guidelines for fortified field spikes that fall outside the recovery limit.

4. Back-up samples are collected directly in series behind the primary sample using the same sampling pump. Back-up samples are collected to evaluate for potential MITC breakthrough in the field samples. Recovery of MITC levels on the back-up samples that are greater than 25% of the levels found in the primary sample would indicate sample breakthrough. Since breakthrough will result in an underestimation of MITC ambient concentrations, any determined breakthrough would trigger an evaluation of the potential effects on the results of the study and can lead to a sampling method re-evaluation.
MITC residue data will be considered valid if it is collected from an air sampler pump measured with less than a ±10% difference in starting and ending flow rates. Manufacturer-certified primary gas flow calibrators will be used to measure the air sampler pump flow rate. The pre-holding time of the XAD-4 sorbent media tubes used for sampling is four years from the time of manufacture. The sorbent media is manufactured and placed inside glass tubes which are sealed at each end by the manufacturer. The glass tubes will be broken only immediately prior to scheduled sampling.

1.5.2 Quality Assurance

The CDFA Center for Analytical Chemistry’s laboratory will follow DPR’s standard laboratory quality control procedures (Segawa 1995). The laboratory currently has a validated method for the determination of MITC in air by GC with a nitrogen-phosphorous detector (Lee 2004). The laboratory previously conducted trapping efficiency tests to ensure breakthrough of the sorbent tubes being used in this study (SKC Inc.® # 226-16-02) does not occur and found that no breakthrough was detected at 100 µg/sample (DPR 2005; see Appendix D). Furthermore, based on previous ambient air monitoring studies conducted in a similar high MITC-generator use region during the high-use period, ambient MITC concentrations to be measured in this study are expected to be below the 100 µg/sample level (ARB 2003). Nevertheless, to assess for potential sample breakthrough of the collected ambient air samples in this study, back-up sorbent tubes comprising of 10% of the total number of primary and spike samples will be collected and analyzed to assess for potential sample breakthrough (Table 5).

Sorbent tubes are certified clean by the manufacturer, SKC Inc®, who holds certificates of registration to various manufacturing standards and provides certificates of quality for their products. Storage stability tests have previously been performed and an acceptable holding time of 60 days was determined (Segawa 1995). Storage stability results from these tests are presented in Appendix C. Table 6 summarizes the holding times and preservation temperatures to be used in this study. The aforementioned quality control samples also will contribute to quality assurance of the reported data.

<table>
<thead>
<tr>
<th>Table 6. Summary of Holding Times and Storage Temperatures.</th>
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</thead>
<tbody>
<tr>
<td><strong>Pre-Holding Time</strong></td>
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<tr>
<td><strong>Holding Time</strong></td>
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<tr>
<td><strong>Storage and Transport Time</strong></td>
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<tr>
<td><strong>Storage Temperature in Field</strong></td>
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<tr>
<td><strong>Storage Temperature at Warehouse</strong></td>
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<tr>
<td><strong>Storage Temperature at Laboratory</strong></td>
</tr>
</tbody>
</table>

1.6 Training

1.6.1 Training Requirements

DPR Environmental Monitoring (EMON) personnel are fully trained in conducting ambient air monitoring, sample collection and transport due to prior training for other air monitoring studies conducted by the Department. However, if necessary, DPR will conduct in-house training of its personnel to ensure successful collection of ambient air samples.

CDFA lab staff is already fully trained in the methods for quantifying MITC from ambient air samples (Lee 2004).
1.7 **Documents and Records**

1.7.1 List of Forms and Filing Procedures for Paper Files and Records

Prior to sampling, all personnel involved in the study will receive the most current approved version of this QAPP. Due to the study’s short duration (i.e., 12 weeks), DPR does not foresee a need to update this document once approved and thus no need for version control.

When air sampling commences at each monitoring site, the sample tracking number, date, time, staff initials, weather conditions, and air sampler flow rate will be documented on a chain of custody (COC) form as presented by Ganapathy (2004). Collected air samples will be transported under dry ice (-80°C) to EMON’s receiving warehouse located at 3971 Commerce Drive, Suite D West Sacramento, Ca 95691, where they will be logged and kept frozen at -20°C until transfer to the CDFA laboratory for analysis.

Samples received at the CDFA laboratory will be logged into the laboratory information database and assigned unique laboratory identification (ID). The temperature and conditions of the sample at the time of receipt will be recorded. Sample processing procedures will be performed according to the appropriate CDFA procedural standard operating procedures (SOPs); the dates, times, and analyst(s) initials will be recorded.

At the CDFA lab, all data undergoes a technical peer review by multiple analysts, and a complete review of the full analytical data package is performed by the laboratory supervisor before signature and release of the summary data report to the DPR laboratory liaison. The laboratory liaison performs a third-level administrative review of the summary data report, which includes a check of sample dates (dates of submitted samples align with scheduled sampling days), analyses performed versus the Analysis Request Sheet and COC, and evaluation of current data versus the historical analytical data maintained by CDFA.

Also see Bradley (1997) for details regarding storage of data.

1.7.2 Electronic Record Keeping--Forms

Electronic data will be stored on the instrument data station at CDFA for a period of two years, after which time it may be purged if disk space is needed for other data. Results from the study will be entered into an electronic spreadsheet by the study leader and stored both on the physical hard drive of the workstation and on DPR’s network server for backup.

2 **Data Generation and Acquisition**

EMON staff conducting ambient air sampling and collection of samples will follow the guidelines outlined here.

2.1 **Sampling Design**

DPR will select communities for this study based on reported MITC use, access to the potential monitoring site, and ability to obtain permission for use of the site. Within a selected community,
monitoring site preference will be given to schools, civic offices, fire and police stations or other public buildings, near the edge of the community and downwind of high use areas.

The location and siting criteria for the air sample inlet will meet all following U.S. EPA ambient air siting requirements (40 CFR Part 58):

- 2 to 15 meters above ground
- At least 1 meter horizontal and vertical distance from supporting structure
- Should be at least 20 meters from trees
- Distance from obstacles should be at least twice the obstacle height
- Unobstructed air flow for 270°

Sampling dates and times will be evenly distributed throughout the week in order to cover a variety of dates and times. See Table 5 in Section 1.4 for proposed sampling dates.

### 2.2 Sampling Methods

#### 2.2.1 Sample Collection

Equipment will include personal sampling pumps (SKC Inc® models PCXR4 and PCXR8), necessary tubing (Tygon®), manufactured pre-packed 200/1800 mg coconut charcoal tubes with sealed glass end tips (SKC Inc® # 226-16-02), grounded and polarized electrical power cables, and appropriate enclosures which provide both security and protection from the environment for equipment.

Sampler flow rates will be calibrated during field deployment and will be checked at the beginning and end of each sampling period. The air sampling pump should be measured to ensure it has a difference no greater than ±10% between starting and ending flow rates for the sample to be considered valid. The target sample flow rate will be 1.5 liters per minute (LPM). Sampling will follow the guidelines outlined in the SOP, “Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps” (EQAI001.00, see Appendix B) (Wofford 2001).

COC forms will be completed in the field with information on sampler location, date, start/stop time, initial and final flow rates, sample media ID, analyst/sampler name, and comments about any unusual conditions that occurred in the field.

#### 2.2.2 Equipment Decontamination

Since ambient air is to be passed through the sampling equipment, no decontamination is necessary as there will be no direct exposure to any applied pesticides. Possible modes of contamination within the laboratory have been discussed and are highly improbable (Segawa 2012, Wright 2012). Thus, decontamination at the CDFA analytical laboratory is not of concern or necessary.

### 2.3 Sample Handling and Custody Requirements

Samples will be collected in conjunction with a Chain of Command record. A COC is an appropriate format to record important data associated with each individual sample. Normally, a COC is used to record three types of information: field information, laboratory information, and information about the personnel who handle the sample. See Ganapathy (2004) for more details.
2.3.1 Sample Custody, Sample Shipping, Chain of Custody Procedures

Samples will be recovered by EMON personnel and shipped with a completed COC record to the DPR sample receiving facility. Immediately after collection, samples will be stored on dry ice in an insulated container until they arrive at the sample receiving facility, where they will be stored in a freezer at or below zero degrees Fahrenheit until transferred to CDFA. Samples will not be stored for longer than two weeks prior to shipment to the CDFA laboratory for analysis.

A COC will be created for each sample and has three sections: field information, lab information, and the signatures of the people who handle the sample. The COC must contain places to enter the following field information: study number, sample number, sampling date, and type of sample. The COC must contain places for all people who handle the sample to sign his/her name. This is a record of persons who had custody of the sample during all steps of the process from container preparation, sample collection, sample storage and transport, and sample analysis.

The person who prepared the sample container will sign the first “relinquished by” line. The “received by” line will be signed and dated by the person collecting the sample. That same person then will sign to relinquish the sample when it is delivered to the sample storage facility. The person who transports the sample to the laboratory will sign the COC last. All signatures must be in ballpoint pen followed by a date and time that the COC was signed. No erroneous information may be erased on the COC. Errors must be lined out and initialed, and the correction written in. See the Appendix A for the COC form to be used in this study.

See Jones (1999) and Ganapathy (2004) for complete SOPs on this topic.

2.3.1.1 Shipping Procedures

Samples will be placed in an insulated shipping container immediately after sampling in the field and surrounded with sufficient dry ice to freeze the samples. Chain of custody records must accompany samples at all times. See Jones (1999) for more details.

2.4 Analytical Methods

All ambient air samples will be analyzed at the CDFA’s Center for Analytical Chemistry. MITC will be quantified using gas chromatography- thermionic specific detector (GC/TSD). The reporting limit of MITC is 0.05 µg per sample by TSD (Lee 2004). See the Appendix C for current SOPs on sample analysis.

Residues of MITC adsorbed from ambient air onto activated charcoal are desorbed (extracted) from the charcoal with 0.1% CS₂ in ethyl acetate. They are then analyzed by GC using a thermionic specific detector. To ensure instrument accuracy and precision, a six point standard curve of 0.025, 0.05, 0.10, 0.50, 1.00, and 5.00 µg/mL shall be obtained at the beginning and the end of each set of samples for calculating the response factors and checking performance of the instrument(s). Extraction of adsorbed MITC from sorbent tubes is to occur within seven days of sample submission to the CDFA Center for Analytical Chemistry and results are to be submitted to EMON’s laboratory liaison within six weeks.
2.5 **Quality Control**

See Section 1.5 for details.

2.6 **Instrument/Equipment Testing, Inspection, and Maintenance**

Field equipment will be calibrated at the beginning of each sampling period with primary gas flow calibrators factory-certified with an NIST-traceable calibration by the manufacturer (ISO 17025-accredited facility). Flow readings will be recorded on COCs for every sample. Initial sample flow should be within 10% of the desired flow rate (1.5 LPM). At the end of the 24-hour sampling period, ending flow rates will be recorded on the COC. If the ending flow rate is greater than 10% of the starting flow rate, the sample will be considered invalid and a make-up sample will be taken by sampling personnel.

All analytical laboratory equipment is calibrated as stated by Lee (2004). The testing, inspection and maintenance of all analytical laboratory equipment, and any necessary corrective action will be done under the discretion of the CDFA’s Center for Analytical Chemistry.

2.7 **Instrument/Equipment Calibration and Frequency**

During sample collection, the personal sampling pumps and primary gas flow calibrators will be the only instruments used for data generation or collection activities that may affect quality and must be controlled and, at specified periods, calibrated to maintain performance within specified limits. As already stated, personal sampling pumps are to be calibrated at the beginning of each sampling period with primary gas flow calibrators. The flow calibrators are to be factory recertified annually with an NIST-traceable calibration.

All analytical laboratory equipment at the CDFA’s Center for Analytical Chemistry is calibrated as stated by Lee (2004). All tools, gauges, instruments, and other sampling, measuring, and test equipment used for data generation that may affect quality and must be controlled and, at specified periods, calibrated to maintain performance within specified limits will be done under the discretion of the CDFA’s Center for Analytical Chemistry.

2.8 **Inspection/Acceptance of Supplies and Consumables**

Coconut charcoal sorbent tubes are shipped from the manufacturer to DPR’s warehouse with certificates of quality. Analytical laboratory consumables and supplies are inspected and accepted under the discretion of CDFA’s Center for Analytical Chemistry.

2.9 **Non-direct Measurements**

A source of non-direct measurements for this study will be the PUR database, maintained by DPR. The PUR database will be utilized to determine areas of potential ambient air monitoring based upon reported MITC. Since current auditing procedures for the database already exist, the data will be accepted as is.

Another source of non-direct measurements for this study will be meteorological information obtained from the CIMIS database, which is maintained by the California Department of Water Resources (CDWR). Wind direction and wind speed will be used in this study to prioritize community monitoring...
site locations that are downwind of high MITC use areas. Weather data undergoes various auditing procedures performed by CDWR staff and will be accepted as is.

2.10 Data Management—Electronic Record Keeping

Data will be first generated in the field during sampling set up. Specifically, the date/time/location, sample identification, initial flow rates, etc. will be recorded on the sample COC. Additional data will be after sample collection and also recorded on the COC. Once results are obtained by the analytical laboratory, the mass of MITC per sample will be recorded on the appropriate COCs which are then forwarded to the DPR laboratory liaison.

The laboratory liaison will perform a third-level administrative review of the summary data report which is then forwarded to the study leader. The study leader will then calculate MITC concentrations in ambient air as 24-hr air concentrations by taking the weight of the pesticide analyte per sample medium (result from chemical analysis) and dividing this value by the volume of air pulled through the sample medium over the 24-hr sampling period. Concentrations will be reported in nanograms per cubic meter (ng/m³).

The standard recording-keeping procedures, document control system, and the approach used for data storage and retrieval on electronic media are described by Bradley (1997) and Ganapathy (2004). The control mechanism for detecting and correcting laboratory errors includes the review of results by a second chemist to check for calculation errors. Data handling equipment includes analytical laboratory instrumentation and workstation personal computers. Lee (2004) outlines procedures for addressing data generated as part of the study.

3 Assessment and Oversight

3.1 Assessment and Response Actions

The first assessments will begin in the field by personnel assigned to collect air samples as scheduled. This will include checking and calibrating equipment to ensure samples will be collected according to specified study criteria (e.g., flow rate and duration of collection, see Section 2 of Data Generation and Acquisition for details). These self-assessments will include all personnel assigned to sample collection (See Section 1.2.1 in Table of Responsibilities) and the results of such assessments will be reported to the project leader. No independent assessments will be conducted. Incoming samples to the analytical laboratory and the results of their measurement will be assessed as received and described in Section 1.7.1.

The study leader, in conjunction with the program supervisor and program manager, will provide oversight as needed. Oversight is to include reviews of sampling procedures and techniques, reviews of field data and observations, and assistance to sampling personnel as requested. Due to the short-term nature of the study (12 weeks) no field audits will be performed.

The information expected from the study will be recorded on the COC (date, time, flow rates, etc.) including the results from CDFA’s Center for Analytical Chemistry. Criteria for success include following the procedures outlined in Section 2 of Data Generation and Acquisition and Section 4 of Data Validation and Usability.
3.2 Reports to Management

Only one report to management regarding the study’s results will be made at the conclusion of the study due to its short-term nature (12 weeks). The report will be distributed to both the supervisor and program manager at EMON and also to necessary personnel at the US EPA. Additionally, DPR will post the report to its web site for public viewing (within one year of the study’s conclusion). The report will describe the study’s results and any assessments of data quality and recommended solutions. The study leader will prepare the report, which must undergo a formal review process at DPR.

4 Data Validation and Usability

4.1 Data Review, Validation, and Verification

Data obtained from the analysis of field samples is first reviewed and validated by analytical laboratory personnel as described by Segawa (1995) and Lee (2004). For MITC quantification, upper and lower warning and control limits are set at ±2 and ±3 standard deviations derived from the average percent recovery, respectively, of the above-mentioned replicates. These limits are intended to remain static for the duration of the study, but may be updated if significant changes are observed based on the on-going accuracy and precision data derived from the field and laboratory Quality Control (QC) samples. The upper control limit (3x standard deviation) is approximately 119% recovery and the lower control limit (3x standard deviation) is approximately 73% recovery for GC/TSD.

A summary data report is then forwarded to the DPR laboratory liaison. The laboratory liaison performs a third-level administrative review of the summary data report, which includes a check of sample dates, analyses performed versus the Analysis Request Sheet (also known internally as a “Check-In Sheet”) and COC, and evaluation of current data versus the historical data. Afterwards, the data is sent to the project leader for a final review.

4.2 Verification and Validation of Methods

Verification and validation of the methods used in the study are described by Segawa (1995) and Lee (2004). Briefly, chemistry laboratory quality controls have been established for air studies outlining general method development (use of standard solutions, determination of method detection and reporting limits, method validation, and storage stability), continuing quality control measures (reagent blanks, blank-matrix spikes, confirmation of positive results, and blind spikes) and determination of trapping efficiency. Collected air samples will be analyzed by gas chromatography with a thermionic specific detector (GC/TSD) as described in Lee (2004).

See the Appendix C for complete laboratory SOPs to be used in this study.

4.3 Reconciliation with User Requirements

Results from the study are limited to short-term exposure to MITC for bystanders near the areas of sampling and will not reflect potential acute exposure experienced by applicators and or agricultural workers. Results could be compared to both acute and subchronic health screening levels determined for MITC, 66,000 and 3,000 ng/m³, respectively. However, results cannot be compared to chronic
screening levels due to the short duration of the study. Additionally, results could be utilized to correlate air concentrations with pesticide use and local weather patterns.

Results obtained from the study would not need to be reconciled with the defined requirements if sample collection criteria and results are within assumed parameters. Results will be accepted with high confidence if all aforementioned sampling requirements and QC standards are met. If results are found to be anomalous or otherwise depart from the assumed parameters, backup samples will be analyzed by the analytical laboratory, if available, in an attempt to supplement data.

5 References


DPR (2011). Air Monitoring Network Study: Long-Term Ambient Air Monitoring for Pesticides in Multiple California Communities. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency.


Jones, DA. (1999). Standard Operating Procedure Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency.


## Appendix A

### MITC Seasonal Ambient Air Monitoring

<table>
<thead>
<tr>
<th>Study #</th>
<th>Date Start</th>
<th>Date End</th>
</tr>
</thead>
<tbody>
<tr>
<td>311</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Site:**

**Crew:**

**Sample Number**

**Location Code**

**Machine #**

**Flow Rate On**

**Flow Rate Off**

**Time On**

**Time Off**

**Run time**

**PST**

**PDT**

**Field Notes:**

**Laboratory Results Section:**

- **Lab Number**
- **Analyte**
- **Amount**
- **RL**

```
20     MITC
```

**Lab Notes:**

**Tube Type:**

- **SKC**
- **# 226-09**

- **Supelco**
- **# __________**

- **Hand packed**
- **By: __________**
- **Type: __________**

- **Other**

1. **Sample started**

2. **Sample finished**

3. **Sample transport**

4. **QA staff receiving**

5. **Relinquished to CDFA Lab**

6. **Other**

**Date/Time**

**Extracted by:**

**Date**

**Analyzed by:**

**Date**

**Approved by:**

**Date**

**Method #**

**Confirmation #**

**Received by at lab**

**Date/Time**

**Logged in by lab**

**Date/Time**

---

Chain of Custody (COC) form.
Environmental Hazards Assessment Program (EHAP) organization and personnel, such as management, senior scientist, quality assurance officer, project leader, etc., are defined and discussed in SOP ADMN002.
1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) discusses the calibration and use of SKC Inc. personal sample pumps for collection of air samples.

1.2 Scope

This document will provide specific instructions for the use of SKC Inc. personal air pumps for the collection and estimation of pesticides in ambient air.

2.0 MATERIALS

2.1 Constant flow, battery operated personal sampler (SKC # 224-PCXR8)
2.2 Adjustable low flow tube holders and plastic tubing
2.3 Sample tubes to be used in monitoring study
2.4 External batteries, 6-volt and connector cables
2.5 Film calibrator(s)
2.6 Rotameter
2.7 Tube breakers
2.8 Stakes or tripods
2.9 Extra-large binder clips
2.10 Battery and sample pump rechargers
2.11 A/C adaptors for sample pumps
2.12 Measurement equipment: compass, tape, rangefinder
2.13 Meteorological weather station
2.14 Dry ice and ice chest

3.0 PROCEDURES

3.1 General

Air sampling studies are usually conducted for the purpose of (1) determining the flux rate of a chemical following an application, or (2) estimating ambient air concentrations from off-site movement. The study objectives should be clearly stated in the study protocol so that study methods and sampling procedures may be designed accordingly. The chemical being monitored will determine the sample media and tube type.
3.2 Calibration

Flow rate is determined by the chemical being monitored and duration of the sampling period. The determination of the appropriate flow rate is the responsibility of the study project leader. The SKC personal sampler can be adjusted to sample smooth air flow for high volume flow (750 to 5000ml/min) as in section 3.2.1, or pulseless for low volume flow (5 to 500 ml/min) as in section 3.2.2. Calibration of samplers can be conducted in the laboratory before going to the field using the DryCal® Primary Flowmeters (section 3.2.3) or the Accuflow® film calibrator (section 3.2.2) or.

3.2.1 High flow settings

3.2.1.1 Charge SKC personal sampler pump for a minimum of 14 hours by connecting charger plug to sampler charging jack (Figure 1, #8), unless using AC power to run pump.

3.2.1.2 Remove the protective cap covering the regulator shutoff cap screw (#7). Using a screwdriver, make sure the adjustment screw is down all the way (do not overtighten).

3.2.1.3 Test the SKC personal sampler pump for full charge, unless using AC power, by turning the sampler on using "On" switch (#1). Press the "Hold" key (#2) then the "Flow and Battery Check" key (#3). Adjust the flow to 2 liters/minute using the flow adjustment control (#4 & #5). The LCD display should indicate "battery OK" in the upper left-hand corner. Connect to volt meter to determine the extent of the charge.

3.2.1.4 While in the battery test mode, connect the sample media to be used in the field to the filter housing intake (#6). Connect a flow calibrator to the inlet of the sample media. With the sampler running, adjust the flow to the desired rate using the flow adjustment control (#5). After completing the battery test and flow adjustment, turn off sampler.

3.2.2 Low flow settings (for use with either single or multiple adjustable low flow holders)
3.2.2.1 Charge SKC personal sampler pump for a minimum of 14 hours by connecting charger plug to sampler charging jack (Figure 1, #8), unless using AC power to run pump.

3.2.2.2 Test the SKC personal sampler pump for full charge by turning the sampler on using “On” switch (#1) (Press the “Hold” key then the “Flow and Battery Check” key). Adjust the flow to 2 liters/minute using the flow adjustment control (#4 & #5). The LCD display should indicate “battery OK” in the upper left-hand corner.

3.2.2.3 Adjust the flow to 1.5 L/min (#4 & #5). NOTE: the flow is not critical but must exceed the combined sampling flow by at least 150 ml/min. After completing the battery test and flow adjustment, press the “Flow and Battery Check” key to halt the sampler.

3.2.2.4 Remove the protective cap covering the regulator shutoff cap screw (#7). If the sampler was previously used in the high flow setting, open the regulator shutoff valve by turning the adjustment screw 3 turns counter-clockwise with a small screwdriver. Replace the protective cap.

3.2.2.5 Connect an adjustable flow holder to the tubing attached to the filter housing intake (#6).

3.2.2.6 Connect the sample tube to be used in the field to the rubber or tubing connector of the adjustable flow holder. Be sure the tubing is connected to the correct end of the sample tube (air flow direction may be indicated on side of tube).

3.2.2.7 Connect a flow calibrator to the exposed end of the sample tubes (s). Loosen the anti-tamper cover on the manifold of the adjustable flow holder to expose the manifold’s flow adjustment screw(s). Turn on the sampler and turn the manifold’s slow adjustment screw(s) until the desired flow rate is obtained. Cover the manifold’s flow adjustment screw(s) with the anti-tamper cover and tighten. Turn off the sampler.
3.2.3 Use of the DryCal® Primary flowmeter (5ml to 5000ml or 1L to 30L):

3.2.3.1 Connect tube from flowmeter to intake of sample tube.

3.2.3.2 Press the On button on the top of the flowmeter.

3.2.3.3 Turn on SKC personal sampler pump.

3.2.3.4 Press the Read button on the top of the flowmeter.

3.2.3.5 If the flow reading is more or less than 10% of the target flow, adjust the flow controller until the desired flow rate is reached.

3.2.3.6 Repeat reading to assure accuracy.

3.2.4 Use of the SKC Accuflow® 712 Film calibrator (5 to 5000 ml/min):

3.2.4.1 Fill calibrator with soap solution to bottom of glass tube.

3.2.4.2 Constrict rubber bulb to create film bubble. Push the On/Reset button. Calibrator will read speed of bubble as it passes the two detectors.

3.2.4.3 If the flow reading is more or less than 10% of the target flow, repeat 3.2.4.2 and adjust the flow controller before creating next film bubble until the desired flow rate is reached.

3.2.4.4 Repeat reading to assure accuracy.

3.2.5 Test rotameter against a calibrated sample pump before each study.

3.3 Sampling Site Location

Sampling locations will be determined by the information required to fit the specific needs of the study objectives. For application monitoring, the sampling
STANDARD OPERATING PROCEDURE

Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps

sites should surround the application to coincide with most possible wind
directions and conditions. For ambient air monitoring, the samplers should be
placed at locations relevant to the study. If stakes or tripods are used to hold
samplers they should be securely placed at the location site and identified with a
site location number. The sample pumps are placed at the location and the
sample tubes are secured at a sampling height of approximately 1.2 m (4 ft). If
the sampling location is near an electrical outlet, use the A/C adaptor to supply
energy to the sample pump. For sampling in areas where electrical outlets are
not available, the sample pumps have rechargeable nicad batteries. If the
sample periods are scheduled to last longer than 6 hours, the sample pumps
should be connected to external 6-volt rechargeable gel cell batteries with
cables. The batteries should be exchanged with charged batteries at the
beginning of each sampling period.

3.4 Sampling methods

3.4.1 Immediately before the sampling period, prepare the sample tubes
and attach to sampler in the end of tube connected directly to pump
(#6) during high flow use or to low flow adaptor during low flow use.
Secure sample tube(s) to stakes or supports.

3.4.2 The sample tube media should be protected from direct sunlight by
either covering tubes with aluminum foil or placing extra-large
binder clips over media in tubes. If there is a chance of rain, attach
tubes to stakes so the open end of the sample tube chain is
horizontal.

3.4.3 Turn the sample pump on. LCD reading on pump should be zero.
Note time on the chain of custody (COC). Place the DryCal®
primary flow calibrator or a calibrated rotameter over the intake end
of the primary tube and turn sample pump on. Adjust to within 10%
of desired flow. Remove calibrator or rotameter. Record flow
reading of the COC.

3.4.4 At the end of the sampling period, place the DryCal® primary flow
calibrator or a calibrated rotameter over the intake end of the
primary tube and record the ending flow rate on the COC. Remove
calibrator or rotameter and note LCD reading and time on COC.
Turn sample pump off. All pertinent information should be recorded
3.5 Troubleshooting

If the pump does not run when turned on; check to see if the pump is in "hold" mode and correct, if not then replace the pump. If the pump turns on but does not pull air; check to see if the ball in the pump's rotameter (#4) is moving, if not, turn off pump and shake upside down. If the pump still does not pull air, replace the pump with another pump. If the pump is off when at the end of the sampling period; record exact run time from the LCD display window on the COC and replace pump for next sample period. If the ending rotameter reading is more than 10% from the target flow rate, either recalibrate or replace pump with calibrated pump.

3.6 Meteorological station

For all studies which require weather data measurements, a meteorological station should be set up next to or as close to the field as possible. The station should be placed away from any objects or structures which may impede wind flow. The meteorological sensors should be placed at a height of 10 meters from the ground. The data collection should be tailored to the needs of the study. The set up procedure for the meteorological station is described in SOP EQWE001.00.

4.0 REPORTING REQUIREMENTS

4.1 Chain of Custody

A chain of custody form should be completed for each sample according to SOP ADMN006.1. The following information should be recorded on the chain of custody

4.1.1 Study number

4.1.2 Sample number
STANDARD OPERATING PROCEDURE

Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps

4.1.3 Sample location

4.1.4 Date and time of sampling

4.1.5 Machine identification

4.1.6 Flow rate of sampling pump

4.1.7 Exact run time for sampling pump

4.1.8 Sampling personnel

4.1.9 Identification of field or experimental plot

4.1.10 Chemical to be analyzed

4.2 Ancillary Information

Other ancillary information should be recorded or included in the experimental notebook, including type of application, start of application, duration of application, application rate and total amount of chemical applied. Field applications require a map of the exact sampling location(s) in relationship to field layout, field soil type, weather conditions, application equipment, and specifics of any tarping material. Commodity fumigations require a diagram of fumigation chamber and area, holding time, exhaust type and rate, and commodity information. Structural fumigations require a diagram of structure, exhaust method, holding time, and specifics of covering material.

5.0 SAFETY

Safety equipment should be available to personnel at all times in the field. It is the responsibility of the study field coordinator to determine the appropriate safety equipment necessary for the specific chemical being monitored. If a grab sampling detector tube is available for the chemical being monitored, air concentrations should be determined before working in an area in close proximity to an application. A measurement should be made at a sampling location closest to the application site.
STANDARD OPERATING PROCEDURE

Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps

For Methyl Bromide Monitoring: Prior to any sampling period following application, ambient methyl bromide air concentrations should be determined before working in the area. A measurement should be made at a sampling location closest to the application site with a grab sample detector tube rated to measure concentrations to 0.5 ppm and detector tube pump. Self Contained Breathing Apparatus (SCBA) should be worn in areas determined to have high concentrations of methyl bromide.

6.0 STUDY-SPECIFIC DECISIONS

The following study specific decisions are the responsibility of the study project leader, and should be made in consultation with the study field coordinator, senior scientists, and EHAP Quality Assurance Officer.

6.0.1 Sampling location

6.0.2 Flow rate

6.0.3 Sampling interval duration

6.0.4 Meteorological data

6.0.5 Sampling media
Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps

Figure 1. Low Flow Personal air sampler
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), CH₃ –N=C=S, that have been absorbed from the air onto activated charcoal are desorbed from the charcoal with 0.1% CS₂ 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 ¾” 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% CS₂ in ethyl acetate. The working standards shall be prepared to cover the linear range from 0.005 μg/μL to 5.0 μg/μL.

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 ± 3 °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/µL correlates to the RL of 0.05 µg/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 µm

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(°C/min) Temperature (°C) Time (minute)
Initial 45 1
15 90 4
50 220 6.6
Injector temperature: 200 °C
Detector temperature: 250 °C

Retention time: 3.0 min
Injection Volume: 2.0 µL

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 µm
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 ng/µL 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 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.

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:
(sample peak area) (std. conc. ng/µL) (std. vol. injected) (sample final vol., (mL))(1000 µL/mL)

µg = ---------------------------------------------------------------------------------------------------------

(std. peak area) (sample vol. injected) (1000ng/µg)

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.


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:

16.2 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

<table>
<thead>
<tr>
<th></th>
<th>MITC Spiked (µg)</th>
<th>MITC Found (µg)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL-spke1</td>
<td>0.15</td>
<td>0.1314</td>
<td>87.6%</td>
</tr>
<tr>
<td>MDL-spke2</td>
<td>0.15</td>
<td>0.1292</td>
<td>86.1%</td>
</tr>
<tr>
<td>MDL-spke3</td>
<td>0.15</td>
<td>0.1245</td>
<td>83.0%</td>
</tr>
<tr>
<td>MDL-spke4</td>
<td>0.15</td>
<td>0.1297</td>
<td>86.5%</td>
</tr>
<tr>
<td>MDL-spke5</td>
<td>0.15</td>
<td>0.1191</td>
<td>79.4%</td>
</tr>
<tr>
<td>MDL-spke6</td>
<td>0.15</td>
<td>0.1295</td>
<td>86.3%</td>
</tr>
<tr>
<td>MDL-spke7</td>
<td>0.15</td>
<td>0.1211</td>
<td>80.7%</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.1264</td>
<td>84.2%</td>
</tr>
<tr>
<td>STDEV</td>
<td></td>
<td>0.0048</td>
<td>3.20%</td>
</tr>
<tr>
<td>MDL=3.143xSTDEV</td>
<td></td>
<td>0.0151</td>
<td></td>
</tr>
<tr>
<td>RL*</td>
<td></td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th></th>
<th>MITC Spiked (µg)</th>
<th>MITC Found by Detector 1 (µg)</th>
<th>MITC Found by Detector 2 (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL-spke1</td>
<td>0.10</td>
<td>0.1085</td>
<td>0.0930</td>
</tr>
<tr>
<td>MDL-spke2</td>
<td>0.10</td>
<td>0.1100</td>
<td>0.0915</td>
</tr>
<tr>
<td>MDL-spke3</td>
<td>0.10</td>
<td>0.1190</td>
<td>0.1010</td>
</tr>
<tr>
<td>MDL-spke4</td>
<td>0.10</td>
<td>0.1210</td>
<td>0.1010</td>
</tr>
<tr>
<td>MDL-spke5</td>
<td>0.10</td>
<td>0.1200</td>
<td>0.1015</td>
</tr>
<tr>
<td>MDL-spke6</td>
<td>0.10</td>
<td>0.1165</td>
<td>0.1000</td>
</tr>
<tr>
<td>MDL-spke7</td>
<td>0.10</td>
<td>0.1155</td>
<td>0.1000</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.1155</td>
<td>0.0983</td>
</tr>
<tr>
<td>STDEV</td>
<td></td>
<td>0.0049</td>
<td>0.0042</td>
</tr>
<tr>
<td>MDL=3.143xSTDEV</td>
<td></td>
<td>0.015</td>
<td>0.013</td>
</tr>
<tr>
<td>RL</td>
<td></td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Appendix 1  continued

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

<table>
<thead>
<tr>
<th>MDL-spike</th>
<th>MITC Spiked (µg)</th>
<th>MITC Found (µg)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>0.0865</td>
<td>87.6</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>0.0850</td>
<td>85.0</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>0.0843</td>
<td>84.3</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>0.0845</td>
<td>84.5</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>0.0820</td>
<td>82.0</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>0.0901</td>
<td>90.1</td>
</tr>
<tr>
<td>7</td>
<td>0.15</td>
<td>0.0780</td>
<td>78.0</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.0843</td>
<td>84.3</td>
</tr>
<tr>
<td>STDEV</td>
<td></td>
<td>0.00374</td>
<td></td>
</tr>
<tr>
<td>MDL=3.143xSTDEV</td>
<td></td>
<td>0.01176</td>
<td></td>
</tr>
<tr>
<td>RL*</td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

Appendix 2

Method Validation Data for MITC from NPD

<table>
<thead>
<tr>
<th>Spike Level</th>
<th>Set 1 MITC found (%)</th>
<th>Set 2 MITC found (%)</th>
<th>Set 3 MITC found (%)</th>
<th>Set 4 MITC found (%)</th>
<th>Set 5 MITC found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>83.8</td>
<td>91.2</td>
<td>89.0</td>
<td>104.3</td>
<td>86.4</td>
</tr>
<tr>
<td>3.0</td>
<td>82.4</td>
<td>88.4</td>
<td>96.0</td>
<td>102.8</td>
<td>87.9</td>
</tr>
<tr>
<td>8.0</td>
<td>84.7</td>
<td>85.7</td>
<td>77.0</td>
<td>80.8</td>
<td>80.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Spike Level MITC Spiked (µg)</th>
<th>Set 1 MITC found (%)</th>
<th>Set 2 MITC found (%)</th>
<th>Set 3 MITC found (%)</th>
<th>Set 4 MITC found (%)</th>
<th>Set 5 MITC found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>102</td>
<td>99.0</td>
<td>96.0</td>
<td>99.0</td>
<td>97.0</td>
</tr>
<tr>
<td>0.4</td>
<td>82.5</td>
<td>87.5</td>
<td>87.5</td>
<td>90.0</td>
<td>85.0</td>
</tr>
<tr>
<td>3.0</td>
<td>97.3</td>
<td>106.7</td>
<td>103.3</td>
<td>93.0</td>
<td>112.7</td>
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<tr>
<td>8.0</td>
<td>97.8</td>
<td>98.5</td>
<td>92.3</td>
<td>86.9</td>
<td>100.3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Spike Level MITC Spiked (µg)</th>
<th>Set 1 Recovery (%)</th>
<th>Set 2 Recovery (%)</th>
<th>Set 3 Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>81.2</td>
<td>81.1</td>
<td>78.3</td>
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<tr>
<td>10.0</td>
<td>76.7</td>
<td>78.2</td>
<td>78.8</td>
</tr>
<tr>
<td>100.0</td>
<td>77.8</td>
<td>73.7</td>
<td>78.8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Tube size</th>
<th>Samples</th>
<th>Day 0 1/22/07</th>
<th>Day 1 1/23/07</th>
<th>Day 7 1/29/07</th>
<th>Day 14 2/5/08</th>
<th>Day 29 2/20/07</th>
<th>Day 46 3/9/08</th>
<th>Day 60 3/23/09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>QC Blank</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SKC226-09</td>
<td>QC Spike</td>
<td>88.7%</td>
<td>96.7%</td>
<td>86.0%</td>
<td>91.3%</td>
<td>91.0%</td>
<td>91.3%</td>
<td>81.7%</td>
</tr>
<tr>
<td></td>
<td>Spike 1</td>
<td>84.4%</td>
<td>83.0%</td>
<td>78.4%</td>
<td>78.6%</td>
<td>78.4%</td>
<td>79.2%</td>
<td>74.2%</td>
</tr>
<tr>
<td></td>
<td>Spike 2</td>
<td>81.8%</td>
<td>82.6%</td>
<td>79.4%</td>
<td>75.4%</td>
<td>77.0%</td>
<td>78.0%</td>
<td>74.2%</td>
</tr>
<tr>
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<td>Spike 3</td>
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Original method was written by Paul Lee.

Revised By:
Original Signed by: 1/3/2012
__________________________________________
Jean Hsu
Environmental Scientist

Revised By:
Original Signed by: 1/3/2012
__________________________________________
Jane White
Staff Environmental Scientist

Approved By:
Original Signed by: 12/19/2011
__________________________________________
Steve Siegel
Sr. Environmental Scientist

Approved By:
Original Signed by: 12/21/2011
__________________________________________
Elaine Wong
Environmental Program Manager I
## Revision Log:

<table>
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<tr>
<td>9/20/04</td>
<td>Formatting to ISO format</td>
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<tr>
<td>9/20/04</td>
<td>Adding a new instrument (Varian TSD) and the parameters to the method</td>
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<tr>
<td>9/20/04</td>
<td>Reducing reporting limit to 0.05 μg from 0.2 μg</td>
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<td>9/20/04</td>
<td>Adding new validation data obtained from TSD to the method</td>
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<tr>
<td>9/20/04</td>
<td>Modifying the confirmation MSD method parameters</td>
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<tr>
<td>6/08/11</td>
<td>Adding the extraction procedure and validation data for analysis of MITC in the SKC 226-16-02 charcoal tube</td>
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## Study 230-- MITC Trapping Efficiency in SKC coconut charcoal (226-16-02 and 226-09), 24hr
Conducted 12/13/05

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<tr>
<th>Sample #</th>
<th>Machine type</th>
<th>Run Time</th>
<th>Flow Rate</th>
<th>Spike Level</th>
<th>Recovery (ug)</th>
<th>Recovery B [%]</th>
<th>Breakthru</th>
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<th>Recovery (ug)</th>
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Average %Recovery Big Tube 79.0
1.5 L/min 82.3
1L/min 75.8

Average %Recovery Small Tube 80.5
1.5 L/min 80.6
1L/min 80.5

Extracted by: Teresa Woronieka, Suzanne Matsumoto
Analyzed by: Jean Hsu

Staff: PW, CG, PG

Continuing QC spiked at 5 ug =88.6% for big tube, 89.2% small tube