

Monitoring and Laboratory Division  
Air Quality Surveillance Branch

**Sampling Protocol for Methyl Iodide Application Monitoring**

October 22, 2009

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**Signatures:**

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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## **1.0 Introduction**

At the request of the California Department of Pesticide Regulation (DPR), (December 15, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff will monitor one application site for methyl iodide (Iodomethane, CH<sub>3</sub>I). This application monitoring study will be performed during an application of methyl iodide. Methyl iodide application monitoring is requested by DPR to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of methyl iodide as a selective commodity fumigant.

The laboratory analysis method titled "Standard Operating Procedure Sampling and Analysis of Methyl Iodide" dated September 2009, is included as Appendix A.

## **2.0 Project Goals and Objectives**

The goal of this monitoring project is to collect and measure methyl iodide concentrations in ambient air during an application.

To achieve the project goal, the following objectives should be met:

1. Appropriate application of sampling/monitoring equipment to determine ambient methyl iodide concentrations at a site located by DPR.
2. Application of relevant quality assurance/quality control practices to ensure the integrity of field samples.
3. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant data for this project.

### **3.0    Contacts**

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## **4.0 Study Location and Design**

Methyl iodide is a pre-plant biocide used to control insects, plant parasitic nematodes, soil borne pathogens, and weed seeds. It is a fumigant pesticide, and is proposed to be used as a replacement for methyl bromide. DPR recently approved several field research studies of this pesticide although it has not been registered for use in California. In the event DPR registers methyl iodide, they expect use to be high, and might request further extensive monitoring.

### **Study Location**

The field site for the application of methyl iodide was determined by DPR. The application field is located near 20594 Spence Rd, Corral de Tierra, CA 93908 (Figure 1). For this application, methyl iodide will be applied to a 450 x 95 ft plot. The method of application will be a drip application to tarped beds. The rate will be 200 lb/ac of Midas Gold-EC, which consists of approximately 63 lbs/ac of methyl iodide, plus 127 lbs of Chloropicrin and 10 lbs of emulsifier.

### **Study Design**

DPR will document information pertinent to the fumigation of methyl iodide, including the location, size, and configuration of the site, as well as all other fumigations in use in the same area for the prior two weeks. DPR will document the application method, date, time, rate and total amount of methyl iodide used, and tarp model and manufacturer.

ARB and DPR will conduct the methyl iodide monitoring by two different methods: canisters and sorbent tubes, respectively. Samples will be collected at 4 points around the application area during 4 time periods (12 hrs for each sample), for a total of approximately 48 hours. DPR will compare the measured methyl iodide air concentrations using two methods and decide the efficient sampling method for methyl iodide monitoring.

### **Sampling Method**

For each of sampling method, 4 samplers will be positioned around the application, one on each side or corner of the field. The samplers will be placed approx. 25 feet (or further, as required) from the edge of the application area. Samples will be collected during four 12 hour time periods, for a total of 16 samples (plus spikes, blanks, and collocated samples) for each method.

The sampling/analysis method developed by the ARB Northern Laboratory Branch Special Analysis Section utilizes Silco canisters (Appendix A). During this study, a canister sampler will be used (Tisch TE-323), enabling field staff to program equipment for unattended start and stop activation. The sampler can accommodate up to three (3) canisters for unattended sequential sampling. Canisters can be filled up to one (1) atmosphere above ambient. The target final canister pressure will be 10 psig,  $\pm 5$  psig.

Samples will be collected by pressurizing ambient air into a Silco canister. Approximately 3 lpm of air is pulled through the Tisch TE-323 inlet. By adjusting a turn style valve, a regulated portion of the 3 lpm air flow is forced into the sample canister. The inlet heights will be placed at approximately 1.5 meters above the ground.

Because the Tisch sampler can only be configured to sample three (3) canisters with each setup, the study will be divided into two (2) sampling episodes: Background & Fumigation.

Four samplers will be positioned around the application field. One sampler will be located at approximately the midpoint of each side, or at the corners, of the field. A fifth and sixth sampler will be collocated at the expected downwind side (or corner) for a field spike sample and a collocated sample. For each sampling period, one (1) trip spike and one (1) trip blank will be included.

DPR will set up a similar method using sorbent tubes, collocated with the above Tisch samplers.

Background sampling: Four (4) primary samplers, one (1) collocated sampler and one (1) field spike sampler will be deployed prior to methyl iodide fumigation. The four (4) primary samplers will be placed approximately 25 feet away from each side (or corner) of the field. One (1) field spike sampler and one (1) collocated sampler will be located at the expected downwind location. Sampling will occur concurrently. During the Background sampling, one field spike ( $5 \mu\text{g}/\text{m}^3 \text{CH}_3\text{I}$ ,  $\pm 50\%$ ) will be utilized. Sample duration will be configured for a 12 hour period. One (1) trip spike and one (1) trip blank will accompany the background samples to the field and back to the Laboratory. Background air sampling will be completed approximately an hour (1) prior to the application.

Fumigation sampling: Four (4) primary samplers, one (1) collocated sampler and one (1) field spike sampler will be deployed during the methyl iodide fumigation. The four (4) primary samplers will be collocated to the DPR samplers. One (1) field spike and one (1) collocated sampler will be located at the expected downwind location. Sampling will occur concurrently. Sample duration will be configured for three 12-hour periods. One (1) trip spike and one (1) trip blank will accompany the fumigation samples to the field and back to the Laboratory.

The duration of the fumigation process lasts approximately an hour, up to four hours. The application will occur during the first 12 hours of the three fumigation sampling period. The fumigation sampling periods will have staggered start times to coordinate with DPRs sampling start times.

Every attempt will be made to shield all sampled canisters from direct sunlight to help reduce sampled methyl iodide losses. When possible, sampled canisters will be removed from the samplers and stored in a cool shaded location until they can be transported back to the Laboratory in Sacramento. Transportation of sampled canisters to Sacramento will occur as often as feasible during regular working hours.

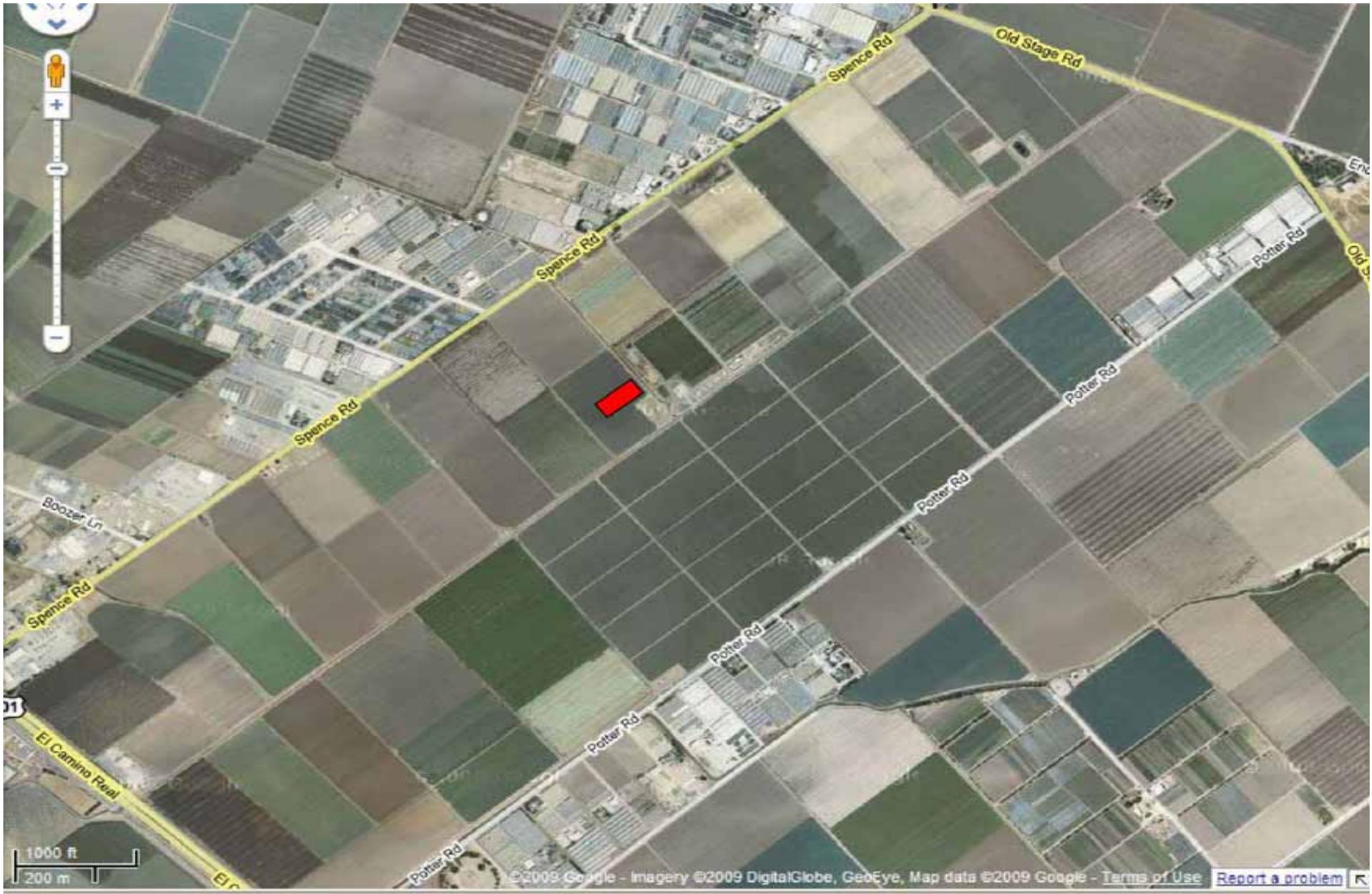


Figure 1: Location of the application field.

**TABLE 1: Guidelines for Sampling Schedule**

<b>Sample period:</b>	<b>Sample duration time:</b>
Background- ~6pm-6am	6 canisters (total) – 12 hours each
Trip	4 canisters (total) – 2 trip spikes, 2 trip blanks
Fumigation- ~8am-8pm (ending on the following day)	18 canisters (total) – 12 hours each

**TABLE 2: Number of Canisters needed**

<b>Canister Type:</b>	<b>Total Number of Canisters needed:</b>
<b>Spikes</b> (5 µg/m <sup>3</sup> CH <sub>3</sub> I, ±50%)	<b>7 canisters</b> (total) – 4 sampled for 12 hours each, 2 trip spikes, 1 spare
<b>Empty</b>	<b>25 canisters</b> (total) – 20 sampled for 12 hours each, 2 trip blanks, 3 spare

### Data Analysis

DPR will compare the methyl iodide concentrations by the two different methods to test if the two sampling methods can detect the chemical at the same concentration levels. If not, the regression between results of the two methods will be statistically analyzed. The correlation between two methods will also be estimated to demonstrate if they exhibit the same concentration trend along the sampling intervals.

## 5.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will transport cleaned and evacuated canisters from MLD's laboratory in Sacramento to the sampling location, and following sample collection, the canisters will be returned to MLD's Sacramento laboratory. These samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

Prior to removing each sampled canister, the operator will assure that the canister valve is securely closed and the corresponding sample paperwork is complete. The collected canisters will be stored in a cool shaded location until they can be transported back the Laboratory. When received by the Laboratory, the canister samples will be analyzed as soon as possible.

All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will provide SPM with cleaned and evacuated Silco canisters, in addition to preparing the necessary canisters spiked with methyl iodide. NLB will perform analyses necessary to measure for methyl iodide concentrations in the sampled canisters and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of Methyl Iodide) in Appendix A.

The following Silco canister validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time:** Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established hold time will be invalidated by the Laboratory.
2. **Duplicate Analysis:** Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL):** MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.
4. **Analytical Linear Range:** Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

## 6.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Measuring Wheel
(1)	200 ft measuring tape
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-100 cc/min
(7)	Tisch TE-323 canister samplers
(18)	Sampling inlets (from Tisch to canister)
(6)	DC power cables for Tisch
(6)	Inlet tubing with particulate filter
(6)	Spare particulate filters
(10)	Spare Swagelok/Parker connectors
(6)	Plastic sheeting to wrap analyzers
(32)	Silco canisters (See Table 2 – 25 clean, 7 spikes)
(32)	Sample sheets for each canister
(6)	Tables
(45)	Batteries (12 [2 each] for Background, 30 [5 each] for Fumigation, 3 spares)
(45)	Battery jumper cables
(2)	Hard hat for each individual
(1)	Box of laboratory quality gloves
(2)	Flashlights
(10)	Batteries for flashlights



## 7.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. State of California, ARB certified transfer standards will be used to measure sample flow rates.

At the request of DPR, metrological sensors will not be utilized.

Each Silco canister will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

**Field Spike (FS):** A field spike will be prepared by the laboratory by injecting a known concentration of methyl iodide gas into a cleaned and evacuated Silco canister. The field spikes (4 total) will be positioned in parallel with the primary samples. The field spikes will be removed and handled identically to the other samples.

**Trip Spike (TS):** A trip spike will be prepared by the laboratory by injecting a known concentration of methyl iodide gas into a cleaned and evacuated Silco canister at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler and not sampled.

**Trip Blank (TB):** A trip blank will be a cleaned and evacuated Silco canister transported to the field and returned to the Laboratory unopened and unsampled.

**Collocated (CO):** A collocated (side-by-side) air sampler will be operated exactly the same as the primary sampler and will be installed alongside the predominantly downwind sampler.

### Site/Sample Identification

The methyl iodide application sampling sites will be named accordingly for the fumigation as follows:

#### Site Naming Examples:

N-F-1 = North side fumigation  
Period 1

W-F-1-CO = collocated west side  
Period 1

S-F-3 = South side fumigation  
Period 3

#### Letter Abbreviations as follows

N = North Side

W = West Side

S = South Side

E = East Side

CO= Collocated

F = Fumigation

FS = Field Spike

TS = Trip Spike

TB = Trip Blank

BK= Background Sample

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will ensure accurate field and lab data collection.

## **8.0 Deliverables**

### **8.1 Air Quality Surveillance Branch Deliverables**

Within 90 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

- 1) Sampling Protocol
- 2) Personnel Contact List
- 3) Site Photographs
- 4) Sample Summary Table
- 5) Field Sample Log
- 6) Laboratory Analysis Reports with calculations in electronic format
- 7) Disk containing electronic files of Report

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

## 8.2 Northern Laboratory Branch (NLB) Deliverables

Within 90 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

- 1) Table(s) of sample results to include:
  - a. Sample identification (name)
  - b. Date sample received from field
  - c. Date sample analyzed
  - d. Dilution ratio
  - e. Analytical results
- 2) All equations used in calculating analytical results.
- 3) Table of duplicate results including calculated relative percent difference (RPD) when applicable.
- 4) Table of collocated results.
- 5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries when applicable.
- 6) Table of analytical results from all trip blanks.
- 7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries when applicable.
- 8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
- 9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

**APPENDIX A:**  
**Standard Operating Procedure and Analyses for Methyl Iodide**

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methyl iodide collected by Silco canister method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of Methyl Iodide.

California Environmental Protection Agency

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 **Air Resources Board**

**Standard Operating Procedure  
Sampling and Analysis of Methyl Iodide**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

September 2009

Version 1

Approved by:

Russell Grace, Manager  
Special Analysis Section

This report has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

## 1. SCOPE

This method is for the sampling and analysis of methyl iodide in air samples using a six-liter Silco™ canister for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry using an automated cryogenic sampler.

## 2. SUMMARY OF METHOD

Air samples are collected in evacuated six-liter Silco™ canisters. The samples are collected automatically using a Tisch Environmental automatic sample collection system. Final pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. The estimated quantitation level (EQL) for this method is approximately 0.1 parts per billion (ppb).

## 3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. A system blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

## 4. EQUIPMENT AND CONDITIONS

### A. Instrumentation

- Agilent Technologies 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10° C, initial time 1 minute, to 80° C @ 10° C/min, to 200° C @ 25° C/min, hold 1 minute, to 240° C @ 50° C/min, hold 2 minutes.
  - Inlet temperature 150° C; split ratio 44.1:1.
- Agilent 5973 mass selective detector (MSD):
  - Acquisition Mode: SIM
  - Tune File: PFTBA Autotune
  - Ions Monitored: 141,142,144,145
  - Quant Ion: 142
  - Internal Standard Ion: 145
  - Solvent Delay: 3.00 min.
- Wasson ECE cryogenic concentrator with Naffion dryer:
  - Cryo Temp #1 at -170°C
  - Cryo Temp #2 at -150°C

- Sample Oven at 200°C
- Transfer Line Temperature at 150°C
- Mass Flow at 35 ml/min
- Line Purge Time 30 seconds

B. Auxiliary Apparatus

Restek six-liter Silco™ canisters with Silco™ valves

C. Reagents

Calibration Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX47999.

Internal Standard: Methyl Iodide-d3 gas at 500 ppb Matheson Tri-Gas cylinder no. SX46440.

Lab Control Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX48752.

D. Gases

Helium, grade 5 or better

Liquid Nitrogen at 22 pounds per square inch (psi)

Nitrogen, grade 5

Compressed air, ultra zero

## 5. SAMPLE COLLECTION

- A. Samples are collected in evacuated six-liter Silco™ canisters using a Tisch Environmental automated sampler set to deliver ambient air over a fixed amount of time.
- B. The canisters will be filled so the ending pressure will be above ambient in the range of 5 to 10 psig (psi gauge).

## 6. ANALYSIS OF SAMPLES

- A. Connect each canister to a port on the Wasson ECE cryogenic sample concentrator using a short length of polypropylene tubing. Reserve ports one and two for the blank and calibration standard.
- B. For this method the standard volume will be 400 milliliters.
- C. Perform an initial calibration curve using the following volumes of known concentrations of methyl iodide: 50, 75, 100, 200, 300, 400 milliliters. At least five (5) points must be analyzed to establish a calibration curve.
- D. Prepare a sample sequence for the GC. The sequence should include a system blank and a continuing calibration verification standard (CCV) for every ten (10) samples analyzed. A lab control standard (LCS) should be run prior to field samples to verify that QC criteria have been met.
- E. To minimize excessive carry over of contaminants from one analysis to the next, a system blank should be run more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.

- F. Review and edit the quantitation reports as needed.
- G. Samples with concentration greater than the upper point of the calibration curve must be run at a smaller volume. Every attempt should be made to have the results fall within the upper half of the calibration curve. If running a volume of 50 ml results in a value greater than the upper calibration point, then the sample will need to be diluted with compressed nitrogen. Either add nitrogen to the original canister being sure to record the beginning and ending pressures, or transfer a known amount of sample from the original canister into a clean fully evacuated canister. Pressurize with nitrogen again recording the final pressure.
- H. The final results will be adjusted by an appropriate dilution factor and reported in ppb.
- I. The atmospheric concentration is calculated as follows:

$$\text{Sample Conc. (ppb)} = \frac{\text{Sample Vol. (ml)}}{400 \text{ ml}} \times \text{Instrument Result (ppb)} \times \text{Dilution Factor}$$

## 7. QUALITY ASSURANCE

- A. A system blank must be analyzed with each batch of samples. The system blank is a 400 ml sample from a canister pressurized with grade 5 nitrogen. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, after the calibration curve or CCV, and after every tenth sample in the analytical batch.
- B. Continuing calibration verification will be run at the beginning of the analytical batch, every tenth sample and at the end of the sample batch to verify system linearity. The calibration verification values must be within 25% of the actual value. Calibration of the entire system occurs if the CCV is outside the acceptable limits.
- C. A LCS will be run with every sample batch. The LCS analyte concentration should fall within the lower half of the calibration curve. The LCS stock standard should come from a different source or lot than the daily calibration standard. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.
- D. Run specific quality control samples, such as field spikes, trip spikes, and laboratory spikes prior to the field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over.

## 8. SAFETY

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure. Methyl iodide gas is noted as a carcinogen and toxic at levels greater than 1300 mg/kg of body weight. All prep of standards and expected high samples should be performed in a shielded fume hood.

**APPENDIX B:**  
**Method Development for the Air Sampling and Analysis of Methyl Iodide**

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methyl iodide collected by Silco canister method.

California Environmental Protection Agency

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# Air Resources Board

**Method Development for the Air  
Sampling and Analysis of Methyl Iodide**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

September 2009

Version 1

Approved by:

Russell Grace, Manager  
Special Analysis Section

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## 1. SCOPE

A method was developed for the air sampling and analysis of methyl iodide using a gas chromatograph/mass selective detector (GC/MSD). The 2009 requested estimated quantitation level (EQL) was 0.1 parts per billion (ppb).

## 2. SUMMARY OF METHOD

Application air samples are collected in evacuated six-liter Silco™ stainless steel canisters. The samples are collected using a Tisch Environmental automatic sample collection system. Final canister pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses external standard method for instrument calibration. The estimated quantitation level for this method is 0.13 ppb.

## 3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. A system blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

## 4. EQUIPMENT AND CONDITIONS

### Instrumentation

- Agilent Technologies 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10° C, initial time 1 minute, to 80° C @ 10° C/min, to 200° C @ 25° C/min, hold 1 minute, to 240° C @ 50° C/min, hold 2 minutes.
  - Inlet temperature 150° C; split ratio 44.1:1.
  
- Agilent 5973 mass selective detector (MSD):
  - Acquisition Mode: SIM
  - Tune File: PFTBA Autotune
  - Ions Monitored: 141,142,144,145
  - Quant Ion: 142
  - Internal Standard Ion: 145
  - Solvent Delay: 3.00 min.

- Wasson ECE cryogenic concentrator with Naffion dryer:
  - Cryo Temp #1 at -170°C
  - Cryo Temp #2 at -150°C
  - Sample Oven at 200°C
  - Transfer Line Temperature at 150°C
  - Mass Flow at 35 ml/min
  - Line Purge Time 30 seconds

## 5. METHOD DEVELOPMENT

### A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the methyl iodide instrument reproducibility.

**Table 1: Instrument Reproducibility  
Methyl Iodide**

<b>Concentration</b>	<b>Low</b>	<b>Medium</b>	<b>High</b>
Amount (ppb)	0.0794	0.3666	0.7609
	0.0814	0.3669	0.7766
	0.0803	0.3753	0.7815
	0.0742	0.3700	0.7755
	0.0743	0.3669	0.7826
Average	0.0779	0.3691	0.7754
Standard Deviation	0.0034	0.0037	0.0087
Relative Standard Deviation	4.3949	1.0061	1.1182

### B. Linearity

A six-point external calibration is performed. Calibration standards ranging from at or near the EQL to approximately eight times higher are used. A linear regression with an  $r^2$  of 0.995 or higher is required for a calibration to be acceptable. Continuing calibration verifications (CCV) will be run at the start of each analytical batch and after every tenth sample to verify system linearity. The CCV quantitated value must be within 25% of the actual value.

### C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicate spikes of a low-level standard, the MDL and EQL for methyl iodide is calculated as follows:

**Table 2: MDL and EQL Determination**

Amount (ppb)	0.096, 0.091, 0.092, 0.094, 0.095, 0.082, 0.094
Average	0.092
Standard Deviation	0.005
MDL = 3.143*STD	0.015
EQL= 5*MDL	0.134

The calculated MDL for methyl iodide is 0.015 ppb. The EQL for methyl iodide assuming a 1:1.79 dilution of the sample is 0.13 ppb.

#### D. Storage Stability

Storage stability will be performed in triplicate using evacuated canisters spiked with methyl iodide and pressurized to approximately 7 psi. The project will be run for 28 days during September 2009 with canisters analyzed at 0, 1, 7, 14, 21 and 28 days.