

California Environmental Protection Agency

 **Air Resources Board**

**STANDARD OPERATING PROCEDURE FOR THE
ANALYSIS OF GREENHOUSE GAS COMPOUNDS IN AMBIENT AIR BY
GAS CHROMATOGRAPHY MASS SPECTROMETRY**

SOP MLD070

Revision 0

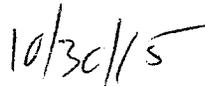
**Northern Laboratory Branch
Monitoring and Laboratory Division**

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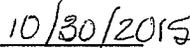


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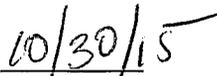
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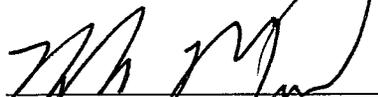
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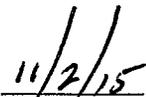
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DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure (SOP) does not constitute endorsement or recommendation of this product by the Air Resources Board (ARB). Specific brand names and instrument descriptions listed in the SOP are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used. This method is restricted to use by or under direct supervision of analysts experienced in the use of air sampling methods and analysis by gas chromatography/mass spectrometry (GC/MS).

TABLE OF CONTENTS

1. Scope	2
2. Summary of Method	2
3. Safety	2
4. Interferences.....	3
5. Apparatus and Equipment	3
6. Reagents and Supplies	3
7. Standards Preparation.....	4
8. Sample Storage and Analysis.....	4
9. Test Sample Preparation	4
10. Instrument Calibration.....	5
11. Analysis	5
12. Quality Control.....	6
13. Calculations	7
14. Reporting Procedure.....	8
15. Preventative Maintenance and Repair.....	8
16. References	8
17. Appendix.....	9

ANALYSIS OF GREENHOUSE GAS COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY MASS SPECTROMETRY

1. Scope

This method describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze greenhouse gas compounds (GHG) in ambient air samples using gas chromatograph/mass spectrometer (GC/MS). See Appendix 2 for a list of compounds that have been validated and found to be applicable to this method. This method is appropriate for concentrations from 0.2 ppbv to 20 ppbv depending on the analyte. This standard operating procedure (SOP) was developed by staff in the Organic Laboratory Section (OLS) of the Northern Laboratory Branch (NLB).

2. Summary of Method

Ambient air samples are collected in summa canisters at monitoring stations located throughout California. Canisters are filled using a pump such as a Xontek 901 or a critical orifice to control flow for a 24 hour timed sample or as a grab sample for special projects with no flow or time control. Grab samples must be pressurized using nitrogen prior to analysis.

Canisters are connected to a GC/MS for analysis via a modified autosampler specifically designed for this use. Using a mass flow controller and timed valve switching, a fixed amount of gas is sampled from the canister through Teflon tubing and trapped on a mixed bed sorbent column. The trapped compounds are released by heating the sorbent column and are recollected on a cryogenic focusing device. The cryogenic focuser is then heated and the compounds are deposited onto the GC column where they are separated and subsequently identified and quantified by the MS.

3. Safety

- 3.1.** This method uses high pressure gases and liquid nitrogen. Follow safe handling practices regarding compressed gases when moving and installing the cylinders. Liquid nitrogen can cause severe freezing and the dewars are heavy. Use suitable equipment and protective devices, such as carts or dollies and thermal gloves, when moving and connecting the liquid nitrogen. Refer to Section III in the MLD Chemical Hygiene Plan for safe handling practices.
- 3.2.** The compounds analyzed by this method are toxic and precautions should be taken to limit the potential for inhalation of these compounds. Refer to safety data sheets (SDS) prior to handling.
- 3.3.** The GC and MS have heated zones which may cause burns. The trap and cryogenic focusing device are both heated and the cryogenic focuser is cooled to

very low temperatures. Avoid contact with these zones and devices when in operation and make certain they are de-energized or at ambient temperature prior to servicing by checking temperature gauges on instruments.

4. Interferences

All target compounds are identified by their mass spectrum and retention times. Compounds having similar GC retention times may co-elute or have ion fragments at the same mass-to-charge ratio (m/z) as the target compound. This can lead to misidentification or inaccurate quantitation. Samples with high concentrations may cause contamination of the analytical system. Analysis of a blank should be done following samples with potentially high concentrations to reduce any possible carryover.

5. Apparatus and Equipment

- 5.1. Summa polished stainless steel canisters
- 5.2. Vacuum source (house or local vacuum pump)
- 5.3. GC modified for the analysis of ambient air
 - 5.3.1. Multiport switching valve for multiple canister connections
 - 5.3.2. Temperature controlled sorbent trap
 - 5.3.3. Cryogenic focuser
 - 5.3.4. Time controlled valves
 - 5.3.5. Nafion Dryer
- 5.4. Mass spectrometer
 - 5.4.1. Electron impact source
 - 5.4.2. Scanning capability of 35 to 500 atomic mass units (amu)
- 5.5. Data station for control of GC, MS, and attached valve switching plus storage and quantification of mass spectral data

6. Reagents and Supplies

- 6.1. Nitrogen ultra-high pure (UHP), 99.999%
- 6.2. Helium ultra-high pure (UHP), 99.999%
- 6.3. Liquid nitrogen
- 6.4. GS-Gaspro column 60 m x 0.32 mm x 1.4 μm or equivalent
- 6.5. FC-43 (Perfluorotributylamine (PFTBA)) or MS tune solution

6.6. Gas calibration standards and controls

6.7. Sorbent trap packing (Carbopack B and C, Carboxen 569 and 1003)

7. Standards Preparation

7.1. When available, certified calibration gas standards are purchased from the National Institute of Standards and Technology (NIST). Calibration and control standards may be purchased from other approved vendors provided they are NIST traceable. Gases provided in cylinders should not be used past the expiration date issued by the vendor unless stability can be verified by comparing historical data. If the pressure in a 30L cylinder is below 500 psi, the standard is no longer valid.

7.2. Gas standards are diluted and humidified in accordance with MLD074 Standard Operating Procedure (SOP) OLS-MLD074-Mixer/Diluter. Standards transferred to a canister have been shown to be stable for at least 30 days. The standard canister must be replaced when it shows degradation on the GC/MS.

8. Sample Storage and Analysis

8.1. All samples are stored at room temperature.

8.2. Samples must be analyzed within 120 days of sampling.

9. Test Sample Preparation

9.1. Samples and standards in canisters must be equilibrated at laboratory room temperature for at least 24 hours prior to analysis.

9.2. Samples taken for analysis are to be checked out in the Toxics Login Sheet Binder.

9.3. Samples canister pressure must be at least 3-4 psi for analysis. If psi is less than 3 the sample is invalid. If the psi is greater than 16 it should be documented but the sample is still valid. (A 24 hour sample with psi > 16 may be indicative of inconsistent sampling.) Grab samples collected for special studies must be pressurized using nitrogen prior to analysis. This introduces a dilution factor.

9.4. After connecting analytical sample lines to canisters, confirm leak tight connections.

9.5. Create a sample list form on the workstation computer for the samples that will be analyzed.

10. Instrument Calibration

- 10.1. At least annually, and when major maintenance is performed, a linear quantitation curve must be generated using a minimum of 5 concentrations of standards. The recommended range is from the Limit of Quantitation (LOQ) up to 100 times the LOQ. Calibration may be achieved using linear regression with the correlation coefficient (r) equal to or greater than 0.98 ($r^2 = 0.96$).
 - 10.1.1. Preparation of standards used for linearity may be performed using the gas mixer/diluter (see OLS-MLD074-Mixer Diluter).
 - 10.1.2. Alternately, a single concentration may be made and the on-column concentration manipulated by varying the sample time.
- 10.2. Daily calibration is conducted prior to analyzing samples using at least one standard at a concentration within the method's validated range for each target analyte using single point quantitation.
- 10.3. At least annually each compounds' LOQ is calculated in accordance with MLD's QC Manual.

11. Analysis

11.1. Instrument Performance Check

- 11.1.1. The MS must be tuned with calibration gas FC-43 to meet the tuning and standard abundance criteria prior to initiating any data collection. The detector is tuned using the Autotune program. The procedure and the criteria for the FC-43 tune can be found in the GC system manuals.
- 11.1.2. The tune values, with regard to positions and abundance ratios of the tune m/z's and their corresponding isotope m/z's, must be reviewed.
- 11.1.3. The system must be checked for leaks and the electron multiplier voltage must be checked and evaluated. Corrective action must be performed as necessary.
- 11.1.4. The tuning report must be saved and archived with associated sample data.

11.2. Initial Setup

The GC method (.mth), sample list (.smp), and sequence list (.seq) are set up on the MS data station. The details of the GC/MS method are described in Appendix 1.

11.3. Sample Concentration and Analysis

- 11.3.1. Sample canisters are connected to the instrument using teflon tubing attached to the canisters by 9/16 inch fittings.
- 11.3.2. Samples are introduced onto the sorbent trap under control of the MS data station method. The gas and sample flow and automation configurations for the sorbent trap loading steps are described in Appendix 1.
- 11.3.3. After the sorbent trap has finished loading, it is dry purged with nitrogen gas, heated, and the contents are transferred to the cyrofocuser. The cyrofocuser loading and subsequent direct transfer of the trapped sample onto the GC column are described in Appendix 1.
- 11.3.4. The ambient samples are analyzed using the same sample volume as used for the calibration and control standards. A smaller volume is analyzed for samples containing concentrations of target analytes that exceed the linear range of the analysis. Smaller volumes (dilutions) are obtained by reducing the trapping time while keeping the mass flow controller set point constant.

11.4. Injection Scheme

The recommended order of analysis is as follows:

- Liquid nitrogen blank
- Calibration Standard
- Control Standard
- Liquid nitrogen blank
- Set of sample canisters (no more than 10)
- Sample Replicate
- Calibration Standard
- Control Standard
- Liquid nitrogen blank
- Any other lab samples; such as contamination checks

11.5. Instrumental Method

A typical method is shown in the Appendix 1, OLS-MLD070-A1. A list of compounds and LOQs are shown in Appendix 2, OLS-MLD070-A2.

12. Quality Control

- 12.1. Each analytical run of 10 or fewer samples must include the bracketing calibration standards, control standards, and blanks listed in 11.4. A list of possible QC problems and corrective actions are shown in Appendix 3, OLS-MLD070-A3.

12.2. The target analyte concentrations in the blanks must be below the compound's LOQ.

12.3. Calibration Standard

A single point calibration is performed with each analytical batch by analyzing the midpoint calibration standard. Retention times, spectra, and the primary quantitation ion integration for each target analyte in the calibration standard data file shall be thoroughly evaluated. Integration results must be within $\pm 20\%$ of expected value. Associated samples in the batch will be invalidated if calibration standard criteria are not met. The quantitation method must be updated after every run with the new calibration information.

12.4. Control Standard

12.4.1. The method control standard is a canister filled with an alternate source gas mixture to verify the operation of the system. This control contains all target compounds and is used to maintain quality control charts.

12.4.2. Recovery of the control standard compounds must fall within the specified criteria limits of the QC chart as established per procedures described in the MLD QC Manual. If the control standard following a set of samples is outside the control limit, the sample results are invalid. Corrective actions must be taken to bring the system back into control and the samples analyses must be repeated.

12.4.3. Control limits must be reestablished when a series of seven or more control standard results trend in one direction or when a new calibration or control standard is put into use.

12.5. Method Precision

Replicate analyses must be performed on a randomly selected sample within each analytical batch to establish precision. Results must be at least five times the LOQ for comparison and evaluation. The replicate analysis must have a relative difference of no more than the established criteria limit (3 x percent relative standard deviation) when compared to the original analysis. If the above criteria are not met, all samples in the batch must be reanalyzed after investigating and performing corrective actions. If corrective actions are not possible, all samples must be invalidated. For samples that have concentrations less than five times the LOQ, relative difference is not calculated.

13. Calculations

13.1. The concentration of ambient VOCs or control compounds is determined by direct comparison of sample response to standard response.

- 13.2. Calculations are generated by the instrument's data system. All calculations shall be clearly documented and maintained with the data set.
- 13.3. Working standard levels and sample concentrations are expressed in units of parts per billion by volume (ppbv.)
- 13.4. Dilutions must be performed on any sample exceeding the upper calibration by more than 10%. If dilution is required, a smaller aliquot of the sample is reanalyzed and the final concentration is calculated by multiplying the compound's concentration by the dilution factor.

14. Reporting Procedure

14.1. Identification of Compounds

All target compounds must be confirmed with spectral information from a standard or MS library. Chromatographic peak integrations performed by the analytical software should be reviewed by the analyst. Re-integrations (manual changes to the baseline) performed by the analyst must be documented and retained with raw data.

14.2. Data Transfer to Laboratory Information Management System (LIMS)

All data is transferred from the analytical instrument to the LIMS database. LIMS performs preliminary checks on quality control criteria and flags any out of control data. The analyst will review the data and apply corrective actions as needed.

14.3. Reporting Results

All data will be reviewed by the analyst, peer reviewed, and reviewed by management as per the MLD Quality Control Manual before being released to the client or for entry into the US EPA Air Quality System (AQS) database.

15. Preventative Maintenance and Repair

- 15.1. Preventive maintenance is done on an annual basis on the GC/MS and repairs are done as needed by an approved vendor under contract to MLD or by experienced staff. Any preventive maintenance and/or repairs completed are documented in a log book stored near the instrument or recorded in the instrument electronic log files.

16. References

These documents can be found on the ARB website at
<http://www.arb.ca.gov/aaqm/sop/summary/summary.htm#LSOP>

- 16.1. MLD Laboratory Quality Control Manual, 2015

16.2. OLS-MLD074-Mixer/Diluter, 2014

17. Appendix

1. OLS-MLD070-A1: Typical Instrument Method for MLD070
2. OLS-MLD070-A2: Target Compounds Validated by MLD070
3. OLS-MLD070-A3: Quality Control Parameters and Corrective Actions

APPENDIX 1
OLS-MLD070-A1
Typical Instrument Method for MLD070

Note – these operating conditions are specific to the ARB's use of Varian Model 3800 GC with Lotus Consulting canister autosampler, Saturn Ion Trap MS2000, and MS Workstation.

Instrument Name: Saturn E

Module Address: 44

Middle Valve Oven

Oven Power: On

Temperature: 120 C

Rear Valve Oven

Oven Power: On

Temperature: 120 C

Valve Table

Valve 1: Sample Valve

Initial: Off

0.01 min: On

2.00 min: On

12.00 min: Off

Valve 2: Cold Trap

Initial: SPT Desorb-off

0.01 min: SPT Desorb-off

2.00 min: SPT Trap-on

12.00 min: SPT Trap-on

16.00 min: SPT Desorb-off

Valve 3: Column injection

Initial: Off

0.01 min: Off

2.00 min: Off

12.00 min: Off

16.00 min: Off

19.00 min: Off

19.98 min: On

20.00 min: On

23.00 min: Off

Valve 4: Cryofocuser Trap

Initial: Series

0.01 min: Series

2.00 min: Series

12.00 min: Series

16.00 min: Series

19.00 min: Bypass
19.98 min: Bypass
20.00 min: Series
23.00 min: Series

Front Injector Type 1079-Cold Trap

Oven Power: On
Coolant: On
Enable Coolant at: 200 C
Coolant Timeout: 30.00 min
Temp Rate Hold Total
© (C/min) (min) (min)

Temp.	C/min	min.	Total min.
-20	0	16.00	16.00
120	200	3.30	20.00
300	200	20.00	40.90
200	200	7.60	49.00

Middle Injector Type 1079-Cryofocuser

Oven Power: On
Coolant: On
Enable Coolant at: 220 C
Coolant Timeout: 30.00 min
Temp Rate Hold Total
© (C/min) (min) (min)

Temp.	C/min	min.	Total min.
200	0	10	10.00
-95	200	8.53	20.00
80	200	2.12	23.00
250	200	20.00	43.85
200	200	5.90	50.00

Front Injector EFC Type 3-Helium Flow to Column

Flow Rate Hold Total
(ml/min) (ml/min/min) (min) (min)

1.5 m//min for 47.00 minutes

Column Oven

Coolant: On
Enable Coolant at: 50 C
Coolant Timeout: 30.00 min
Stabilization Time: 0.10 min
Temp Rate Hold Total
© (C/min) (min) (min) Column Oven

Temp.	C/min	min.	Total min.
100	0.0	12.00	12.00

-40	100.0	6.80	20.20
-40	100.0	5.50	25.70
10	100.0	2.20	28.40
110	10.0	5.50	43.90
240	100.0	4.80	50.00

Front Type 11 Detector EFC-Heated Sample lines

Make up Flow: 0 ml/min

H2 Flow: 0 ml/min

Air Flow: 0 ml/min

Middle FID Detector

Oven Power: On

Temperature: 70 C

Electronics: Off

Time Constant: Fast

APPENDIX 2
OLS-MLD070-A2

Target Compounds Validated by MLD070

Compound	LOQ ppbv
Perfluoromethane (CF ₄)	0.2
HFC-125 (C ₂ HF ₅)	0.2
Freon-22 (CHClF ₂)	0.2
HFC-134a (C ₂ H ₂ F ₄)	0.2
Butane ^a	0.2
HFC-152a (C ₂ H ₄ F ₂)	0.2
R-116 (C ₂ F ₆)	0.2
Sulfurhexafluoride (SF ₆)	0.2
R-23 (CHF ₃)	0.2
R-218 (C ₃ F ₈)	0.2

^a measured, not reported to EPA Air Quality System (AQS)
(used as reference to monitor method performance)

APPENDIX 3
OLS-MLD070-A3

Quality Control Parameters and Recommended Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Linearity	5-point calibration curve run at setup, annually, after major instrument modifications or repair	Correlation coefficient (r) of 0.98 or greater	Check integration, reintegrate or recalibrate.
Calibration Check (bracketing standard)	Midpoint calibration standard analyzed daily or with each analytical batch at beginning and end of each run	Beginning and end check must be within $\pm 20\%$ of each other	Check integration, recalibrate or prepare new standard, reanalyze samples not bracketed by acceptable standards.
System Blanks	Analyze with every analytical batch at beginning and end of each run and after suspected high concentration samples	Less than LOQ	Check instrument for possible contamination. Reanalyze all samples in batch.
Control Standards	Analyze with every analytical batch at beginning and end of each run.	Within established limits based on historical data.	Reanalyze all samples in batch. Invalidate results for affected compound in all samples in batch if reanalysis is not possible. Reestablish control limits when a series of 7 or more control standard results trend in one direction.
Replicates	Analyze one replicate pair with every 10 samples.	3 x %RSD	Reanalyze all samples in batch. Invalidate results for affected compound in all samples in batch if reanalysis is not possible.

