





STANDARD OPERATING PROCEDURE FOR THE
ANALYSIS OF GREENHOUSE GAS
COMPOUNDS IN AMBIENT AIR BY GAS
CHROMATOGRAPHY MASS SPECTROMETRY
MLD070
Revision 1.0

Northern Laboratory Branch
Monitoring and Laboratory Division

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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 a 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 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 910 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 are pressurized using nitrogen prior to analysis.

Canisters are connected to a thermal desorption system via an autosampler specifically designed for this use. Using a mass flow controller, a fixed amount of sample is collected from the canister and trapped onto a sorbent trap. The trapped compounds are released by heating the sorbent trap and sent to the GC column where they are separated and subsequently identified and quantified by the MS.

3. Acronyms

Acronym or Term	Definition
AMU	Atomic mass unit
AQS	US EPA Air Quality System
CAS	Chemical Abstracts Service
GC/MS	Gas Chromatograph / Mass Spectrometer
GHG	Greenhouse Gas Compounds
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation

Acronym or Term	Definition
M/Z	Mass to charge ratio
MDL	Method Detection Limit
MLD	Monitoring and Laboratory Division
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
PFTBA	Perfluorotributylamine
PPB	Parts Per Billion
QC	Quality Control
QCM	Quality Control Manual
RL	Reporting Limit
RPD	Relative Percent Difference
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
UHP	Ultra-High Purity

4. Definitions

- 4.1. ANALYTICAL BATCH – A set of prepared samples analyzed together as a group in an uninterrupted sequence.
- 4.2. BLANK – An aliquot of carrier gas which is analyzed and used to monitor the laboratory analytical systems for interferences and contamination.
- 4.3. BREAKTHROUGH –Determination if any amount of sample was not retained in the cold trap during sampling due to compound structure and cold trap contents.
- 4.4. CALIBRATION CURVE – The calibration curve consists of at least five concentrations of a calibration standard that span the monitoring range of interest to determine instrument sensitivity and the linearity of GC/MS response for the target compounds.
- 4.5. CALIBRATION STANDARD – A standard containing the target analytes at a known concentration obtained from a source other than that of the control standard (second source) or from a different lot number. The mid-level calibration standard is analyzed in a GC/MS system that has met the tuning and mass calibration criteria. May be included as the opening, continuing, or closing standard for an analytical sequence
- 4.6. CONTROL STANDARD – A material of known composition obtained (when possible) from a source other than that of the primary calibration standard that is analyzed to verify the calibration.

- 4.7. CARRYOVER – Contamination from an adjacent sample causing false or inaccurate results in the subsequent sample(s).
- 4.8. COLLOCATED SAMPLE – A sample used to assess total precision (sampling and analysis) which is located within a specified radius of the primary sampler. The collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.
- 4.9. DILUTIONS – Dilution is the process of reducing the concentration of a solute in solution, usually by adding more solvent. Dilutions are required when any sample concentration exceeds the calibrated linear range.
- 4.10. DUPLICATE – Two aliquots taken from and representative of the same sample or product and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis.
- 4.11. HOLD TIME – The maximum amount of time a sample or extract may be stored prior to performing an operation. This can be the time from sample collection to extraction, extraction to analysis, or collection to analysis when there is no extraction process.
- 4.12. INTERFERENCE – A substance that is present that can cause a systematic error in measurement in the sample being analyzed. Examples: impurities in the purging/carrier gas, elevated baselines from solvents, reagents, glassware, sampling media, and other sample processing hardware that may cause misinterpretation of the data.
- 4.13. LIMIT OF QUANTITATION - The minimum concentration or amount of an analyte that a method can measure with a specified degree of confidence. The LOQ is equal to five times the standard deviation of the replicate analyses from the MDL determination/verification. LOQ is analyte and instrument specific.
- 4.14. METHOD DETECTION LIMIT – the minimum concentration of a substance that can be measured by a single measurement and reported with 99 percent confidence that the analyte concentration is greater than zero and statistically different from a blank. It is determined from replicate analyses of a sample in a given matrix containing the analyte and sampling media. The procedure used to determine the MDL is documented in the NLB's Laboratory QCM.

- 4.15. REPORTING LIMIT – A number which data is not typically reported below. The RL may or may not be statistically determined, and may be established by regulatory requirements or in conjunction with client or program needs. The RL is equivalent to or greater than the LOQ.

5. Interferences and Limitations

- 5.1. Although studies have shown that the target compounds can be considered stable for 120 days past sampling date in stainless steel canisters, every effort must be made to analyze the sample as soon as possible. Extreme care must be taken to prevent contamination during sample collection, transportation and subsequent analysis.
- 5.2. 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.
- 5.3. The analytical system may become contaminated when samples containing high compound concentrations are analyzed. If there is suspected carryover from a high concentration sample, additional system blanks should be analyzed and verified to have results below the RL prior to reanalyzing the succeeding sample(s).
- 5.4. High boiling point compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column should be baked out to remove these contaminants prior to analyzing samples. The bake out temperature must not exceed the column’s maximum operating temperature.
- 5.5. Use of a water management device such as a Nafion drier may cause a loss of polar compounds. Ensure that any water management device used does not affect recovery of target compounds.

6. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program’s requirements per any applicable State and federal regulations and

guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, waste disposal, and LIMS functionality pertaining to the program. Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e. data for record). Training is documented and maintained by the laboratory supervisor.

7. Safety Requirements

All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan.

- 7.1. This method uses high pressure gases. Follow safe handling practices regarding compressed gases when moving and installing the cylinders. Use suitable equipment and protective devices, such as carts and safety shoes. Refer to Section III in the NLB Chemical Hygiene Plan for safe handling practices.
- 7.2. The compounds analyzed by this method are toxic and precautions should be taken to limit the potential for inhalation of these compounds. Follow proper laboratory safety procedures.
- 7.3. The GC and MS have heated zones, which may cause burns. The trap is both heated and cooled. 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. See applicable instrument manuals for guidance.

8. Hazardous Waste

Hazardous waste associated with this analysis consists of used pump oil. Pump oil is exchanged when serviced, typically on an annual basis. The used oil is collected in a plastic container and stored in the chemical waste unit. It is stored there until removed by the contracted hazardous waste company for disposal.

9. Equipment and Supplies

- 9.1. Summa polished stainless steel canisters
- 9.2. Vacuum source (house or local vacuum pump)
- 9.3. GC modified for the analysis of ambient air
 - 9.3.1. Multiport switching valve for multiple canister connections
 - 9.3.2. Temperature controlled sorbent trap

- 9.3.3. Time controlled valves
- 9.3.4. Water management control, such as a Markes Kori, Nafion drier, or equivalent.
- 9.4. Mass spectrometer (Electron Impact source)
- 9.5. Data station for control of GC, MS, and attached valve switching plus storage and quantification of mass spectral data
- 9.6. GS-Gaspro column 60 m x 0.32 mm x 1.4 μ m or equivalent
- 9.7. Markes sorbent focusing trap U-T16GHG-2S or equivalent.

10. Reagents and Gases

- 10.1. Nitrogen UHP, 99.999%
- 10.2. Helium UHP, 99.999%
- 10.3. Gas calibration standards and controls
- 10.4. PFTBA or MS tune solution

11. Standards Preparation

- 11.1. 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. If used past the expiration, management approval and documentation comparing concentration to historical data is required.
- 11.2. Gas standards are diluted and humidified in accordance with MLD074 when transferred to a canister for daily use. Standards have been shown to be stable for at least 120 days in our studies.

12. Sample Storage and Hold Time

- 12.1. All samples are stored at room temperature.
- 12.2. Samples must be analyzed within 120 days of sampling. If samples are analyzed greater than 120 days from collection, results are flagged and reported.
- 12.3. Retain samples until all analyses are completed.

13. Sample Preparation

- 13.1. Samples and standards in canisters must be equilibrated at laboratory room temperature for at least 24 hours prior to analysis.
- 13.2. Samples taken for analysis are to be signed out in the Toxics Login Sheet Binder which is used to track the analyses completed on each sample.
- 13.3. Samples canister pressure must be at least 5 psi when received from the field operator. If psi is less than 5 the sample is invalid unless it is a grab (non-flow-controlled) sample. 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.)
- 13.4. Grab samples collected for special studies must be pressurized using nitrogen prior to analysis. This introduces a dilution factor. Refer to the SOP MLD074.
- 13.5. Connect analytical sample lines to canisters.
- 13.6. Create a sample list form on the workstation computer for the samples that will be analyzed.

14. Analysis

- 14.1. Instrument Performance Check
 - 14.1.1. The MS must be tuned with calibration gas PFTBA 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 PFTBA tune can be found in the GC system manuals.
 - 14.1.2. 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.
 - 14.1.3. The system must be checked for leaks and the electron multiplier voltage must be checked and evaluated. Corrective action must be performed as necessary prior to analyzing samples. See instrument manual for guidance.
 - 14.1.4. The tuning report must be saved and archived with associated sample data.

14.2. Sample Concentration and Analysis

- 14.2.1. Sample canisters are connected to the instrument using teflon tubing or canister racks.
- 14.2.2. Samples are introduced onto the sorbent trap under control of the thermal desorption instrument. The gas and sample flow and automation configurations for the sorbent trap loading steps are described in Appendix 1.
- 14.2.3. After the sorbent trap has finished loading, it is dry purged with helium gas, heated, and the contents are transferred to the GC. The sorbent trap loading and subsequent direct transfer of the trapped sample onto the GC column are described in Appendix 1.
- 14.2.4. 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 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.

14.3. Injection Scheme

- 14.3.1. The recommended order of analysis is as follows:
 - System blank
 - Calibration Standard
 - Control Standard
 - Method blank
 - Set of sample canisters (no more than 10)
 - Sample Duplicate
 - System blank
 - Closing Standard
- 14.3.2. Multiple sets of 10 or fewer samples may be analyzed continuously depending on autosampler capacity. Each set of samples must be bracketed by a calibration standard. Additional samples, bracketed by a calibration standard, may be added to the analytical sequence as long as analyses will be

completed within 24 hours from the analysis of the first calibration standard in the sequence.

14.4 Instrumental Method

Due to breakthrough of CF₄ in the cold trap, CF₄ is sampled at a lower volume than the other compounds. For this reason, there are two methods associated with this SOP. A typical method is shown in the Appendix 1, OLS-MLD070-A1, including CF₄ settings. A list of compounds and RLs are shown in Appendix 2, OLS-MLD070-A2.

15. Quality Control

15.1. Each analytical run of 10 or fewer samples must include a calibration standard, control standard, blanks, duplicate, and a closing standard as listed in 14.3.1.

15.2. The target analyte concentrations in the blanks must be below the compound's RL.

15.3. Calibration Standard

A single point calibration is performed with each analytical batch by analyzing a midpoint calibration standard that is consistent with that in the yearly linearity study. 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 $\pm 20\%$ and ± 0.300 minutes of the previous calibration standard response. The batch run will be invalidated if calibration standard criteria are not met. If there is enough canister pressure (see section 13.3), samples should be re-analyzed after calibration standard criteria are confirmed to be working.

15.4. Control Standard

15.4.1. 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 QC charts.

15.4.2. The opening control standard compounds must fall within the specified criteria limits of the Control Chart as established per procedures described in the NLB QC Manual.

- 15.4.3. If outside the Control Limits, corrective actions must be taken to bring the system back into control and the samples analyses must be repeated.
- 15.4.4. Control limits must be reestablished when three consecutive control standard results fall between the warning and control limits, or when a new calibration or control standard is put into use.

15.5. QC Parameters and Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Linearity Study	Minimum of 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 Standard	Midpoint calibration standard analyzed at the beginning of each analytical batch	Beginning check must be within $\pm 20\%$ Area Counts and ± 0.300 min of previous valid run.	Check integration, reanalyze standard, or prepare new standard. Reanalyze samples not bracketed by acceptable standards. If reanalysis is not possible, then samples are invalid for impacted analytes.
System Blanks	Analyze with every analytical batch at beginning and end of each run and after suspected high concentration samples	Less than RL	Check instrument for possible contamination. Reanalyze affected samples in batch, if needed.
Method Blank	Analyze once per analytical batch (per Injection Scheme)	Less than RL	Check instrument for possible contamination. Reanalyze all samples in batch, if needed. If reanalysis is not possible, then samples are invalid.
Control Standards	Analyze with every analytical batch at beginning of each run, following the calibration standard.	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 three consecutive control standard results fall between the warning and control limits.

QC Type	Frequency	Criteria	Corrective Action
Duplicates	Analyze one duplicate pair with every 10 samples.	Duplicate must be within $\pm 25\%$ of original for analyte concentrations $\geq 5x$ RL.	Reanalyze all samples in batch. Invalidate results for affected compound in all samples in batch if reanalysis is not possible.
Closing Standard	Analyzed after 10 or fewer samples and at end of analytical batch	Integration results must be within $\pm 20\%$ and ± 0.300 minutes of the calibration standard response. A Closing Standard must be analyzed within 24 hours of first standard.	<ul style="list-style-type: none"> • Evaluate the run to determine if there is compelling evidence the standard was not properly injected. If so, reanalyze once if within the 24-hour clock, and report the second analysis if it is within criteria, and document the reanalysis and issue on the run log and review checklist. • If there is no compelling evidence of a mis-injection or 24 hours has lapsed, reanalyze entire batch back to the last passing standard or invalidate the impacted compound(s) with NLB management approval. • If the reanalysis is outside criteria, prepare new standards and reanalyze entire batch back to the last passing standard.
Hold Time	All Samples	Must analyze within 120 days of sampling.	Samples analyzed outside hold time will be reported and flagged in LIMS.
Canister Pressure	All Samples	Must be at least 5 psi when received from field operator, unless they are grab samples.	Samples under 5 psi will be invalidated in LIMS, unless they are grab samples.

16. Calculations

- 16.1. The concentration of ambient VOCs or control compounds is determined by direct comparison of sample response to standard response. Calculations are generated by the instrument's data system. All calculations shall be clearly documented and maintained with the data set.

$$Concentration_{sample} = \frac{(Concentration_{standard})(Response_{sample})}{Response_{standard}}$$

- 16.2. Working standard levels and sample concentrations are expressed in units of parts per billion (ppb).

16.3.

Dilution factors are calculated as:

$$Dilution\ Factor = \frac{V_f}{V_i}$$

Where:

V_f = Full Sample Volume

V_i = Partial Sample Volume

- 16.4. The RPD between two results is calculated as follows:

$$RPD = \frac{|X1 - X2|}{((X1 + X2)/2)} \times 100\%$$

Where:

X1 = first measurement value

X2 = second measurement value

- 16.5. The Percent Difference calculation for opening and closing standard criteria is as follows:

$$\% \text{ Difference} = \frac{(Area_{New\ Std.} - Area_{Old\ Std.})}{Area_{New\ Std.}} \times 100\%$$

Where:

New Standard is the Opening/Closing

Old Standard is the Previous/Opening (respective).

17. Data Management and Reporting

Data management consists of samples logged into LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are kept with the instrumentation at all times.

17.1. 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.

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

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

17.3. Reporting Results

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

18. Maintenance and Repair

18.1. Preventive maintenance is done on an annual basis on the autosampler, concentrator, and GC/MS. 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 log files.

19. Revision History

	Date	Updated Revision	Original Procedure
0.0	October 30, 2015	Procedures for analysis of GHG	None
1.0	January 14, 2021	<ul style="list-style-type: none"> • Changed from liquid nitrogen to electrically cooled cryogenic trap. • Changed adsorbent trap composition and dimensions. • SOP format changed to comply with SOP template for SOPs. • General QC updates (refer to Section 15.5) 	October 30, 2015

20. References

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

20.1.1. MLD NLB Laboratory Quality Control Manual, current version

20.1.2. MLD074, Standard Operating Procedure for Preparation of Calibration and Control Standards Using a Multi-Component Gas Blending and Dilution System, current version

20.2. NLB Chemical Hygiene Plan, current version

20.3. A Cryogen-Free Method for Monitoring Trace Greenhouse Gases in Air, Note 87a, Markes International, June 2009.

21. Appendices

21.1. OLS-MLD070-A1: Typical Instrument Method for MLD070

21.2. OLS-MLD070-A2: Target Compounds Validated by MLD070

APPENDIX 1

OLS-MLD070-A1

Typical Instrument Method for MLD070

Note – these operating conditions are specific to the ARB's use of Markes Unity 2 TD and Thermo GC/MS.

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Standby – Split On; 5 mL/min
Flow Path – 120°C
GC Cycle Time – 35 minutes

Pre-Sampling Tab:

Leak Test – On
Sample Purge Time – 2.0 minutes at 50 mL/min
Internal Standard – No

Sampling Tab:

Sample by Volume – Yes
Sample Quantity – 150 mL at 50 mL/min
Use Dedicated Purge Channel – No
Post Sampling Purge Time – 1 minute at 50 mL/min
Enable CIA Post Sampling Purge - No

Trap Settings Tab:

Trap Purge – 1 minute at 20 mL/min
Trap Low – -30°C
Trap High – 300°C
Trap Heating Rate – 40 °C/s
Trap Hold – 5 minutes; split off
Post-Desorb Purge – 0 minutes at 50 mL/min

Helium CIA Pressure – approx. 25 psi
Nitrogen Pneumatics – approx. 60 psi
Nitrogen Humid Purge – approx. 15 psi

Note: Due to breakthrough, a second method is used to sample CF₄.

- 1.) Sample Quantity – 25 mL at 20 mL/min
- 2.) GC Cycle Time – 18 minutes

Thermo GC Parameters:

Front Inlet – 200°C
 Front Inlet Flow Mode – FlowCtrl
 Front Inlet Pressure Control – Off
 Front Inlet Flow Control – On
 PrepRun Timeout – 999.99 minutes
 Equilibration Time – 0.100 minutes
 Ready Delay – 0.100 minutes
 Front Inlet Split Mode – Splitless
 Front Inlet Split Flow Control – Off
 Front Inlet Flow – 1.200 mL/min
 GC Standby Temp – 35°C

Thermo Column Oven Parameters:

Retention Time (minutes)	Rate (°C/min)	Target Value (°C)	Hold Time (minutes)
2.000	0.00	35.0	2.00
22.000	4.00	115.0	0.00
33.250	12.00	250.0	0.00

Thermo Column Oven Parameters (CF₄):

Retention Time (minutes)	Rate (°C/min)	Target Value (°C)	Hold Time (minutes)
2.000	0.00	35.0	2.00
5.750	4.00	50.0	0.00
15.750	20.00	250.0	0.00

Thermo MS Parameters:

Ion Source (Thermo MS) – 310°C
 MS Transfer Line – 230°C
 Ionization Mode – EI

Time (minutes)	Range (amu)	Dwell/Scan Time (seconds)	Total Scan (seconds)	Filament On	Detector Gain
2.50	38-150	0.1	0.212	YES	3.00x10 ⁵
	69, 50	0.05	0.212	YES	3.00x10 ⁵
5.90	38-150	0.1	0.104	NO	3.00x10 ⁵
6.40	38-150	0.1	0.104	YES	3.00x10 ⁵

*Same MS settings are used for CF₄ analysis.

APPENDIX 2

OLS-MLD070-A2

Target Compounds Validated by MLD070

Compound	RL ppb	CAS Number
Perfluoromethane (CF ₄)	0.2	75-73-0
HFC-125 (C ₂ HF ₅)	0.2	354-33-6
Freon-22 (CHClF ₂)	0.2	75-45-6
HFC-134a (C ₂ H ₂ F ₄)	0.2	811-97-2
HFC-152a (C ₂ H ₄ F ₂)	0.2	75-37-6

