State of California
California Environmental Protection Agency
Air Resources Board
MLD/QMS-066 (NEW 4/14)

QUALITY MANAGEMENT DOCUMENT ADDENDUM

(District completes Sections 1 through 6 -- please type)

Section 1. ARB Document
☐ Quality Management Plan (QMP)
☐ Quality Assurance Project Plan (QAPP)
☒ Standard Operating Procedure (SOP)

Section 2. District Information		
Agency Name:	Northern Laboratory Branch Monitoring and Laboratory Division	
Agency Address:	1927 13th Street, Sacramento	
Prepared by:	David Wevill, Air Pollution Specialist	
Agency Contact Name/Phone Number:	Patrick Rainey	(916) 327-4756
Agency Signature/Date:	Patrick Rainey	1/3/2025

Section 3. Document Title *(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)*	**Date**
STANDARD OPERATING PROCEDURE FOR ANALYSIS OF VOLATILE ORGANIC AND OXYGENATE COMPOUNDS IN AMBIENT AIR USING GAS CHROMATOGRAPH/MASS SPECTROMETER MLD072 Revision 0.0 with Addendum A36	January 31, 2022

Section 4. Proposed Deviation(s)
(specify exact section(s), page number(s) and language in existing ARB document that your District proposes to modify and then specify proposed modification (including any spreadsheets or forms).

Page 1, Section 3 add:

ICAL	Initial Calibration

Page 2, Section 4.2 states:
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 response for the target compounds.
Replace with:
INITIAL CALIBRATION (ICAL) - Consists of at least five concentrations of a calibration standard that span the monitoring range of interest to determine instrument sensitivity and response for the target compounds.

Page 2, Section 4.6 states:
CHECK / CLOSING STANDARD – A mid-level standard containing the target analytes at a known concentration analyzed at the end of every batch after sample analysis to confirm stability of the instrument. (See Continuing Calibration Verification).
Replace with:
CCV / CLOSING STANDARD – A mid-level standard containing the target analytes at a known concentration analyzed at the end of every batch after sample analysis to confirm stability of the instrument. (See Continuing Calibration Verification).

Page 4, Section 4.18 states:
SYSTEM / METHOD BLANK – An aliquot of nitrogen gas analyzed and used to monitor the laboratory analytical systems for interferences and contamination.
Replace with:
SYSTEM / METHOD BLANK – An aliquot of nitrogen gas or zero air analyzed and used to monitor the laboratory analytical systems for interferences and contamination.

Page 6, Section 9 add:
9.14 Zero air generator (optional, only if using zero air for system / method blanks), Teledyne model T701H, or equivalent.

Page 7, Section 11.2.1 states:
Gaseous standards are prepared with a flow-controlled gaseous mixer/diluter. For each gaseous standard canister prepared, spike the single 6 L canister with 150 µL of reagent grade water. With the canister connected to the gaseous mixer/diluter, set the diluter to the appropriate dilution setting for the gas standard, open the canister to begin filling with the desired gaseous concentration until pressurized to 25 psig. Refer to SOP MLD074 for detailed instructions on operating the diluter. Allow canister to equilibrate overnight before use. Working standards are typically assigned a 60 day expiration date from preparation, but not to exceed the expiration date of the neat standard.
Replace with:
Gaseous standards are prepared with a flow-controlled gaseous mixer/diluter. For each gaseous standard canister prepared, spike the single 6 L canister with 150 µL of reagent grade water. If preparing a canister using multiple cylinder standards, hand spike with the required volume of gas standard using a gas-tight syringe (see Table A).

Table A. Calibration standard preparation examples:

Description	Volume of 100 ppb VOC gas standard	Volume of 1 ppm oxygenate gas standard
Low-level calibration standard	50 mL	80 mL
Mid-level calibration standard	1/50 dilution using mixer/diluter	400 mL
High-level calibration standard	1/10 dilution using mixer/diluter	800 mL
Control standard (Using 2nd source standards)	1/50 dilution using mixer/diluter	400 mL

Next, connect the canister to the gaseous mixer/diluter, set the diluter to the appropriate dilution setting for the gas standard, allow to flush to vent for at least 20 minutes, open the canister to begin filling with the desired gaseous concentration until pressurized to 25 psig. Refer to SOP MLD074 for detailed instructions on operating the diluter. Allow canister to equilibrate overnight before use. Working standards are typically assigned a 60 day expiration date from preparation, but not to exceed the expiration date of the parent standard.

Page 8, Section 14 states:
Blank preparation may be accomplished in two possible ways. A nitrogen cylinder with a regulator or canister filled with nitrogen connected directly to a sample port can be used to achieve a blank analysis. A nitrogen cylinder requires a regulator to control the pressure and flow. Either of these types of blanks must meet the criteria summarized in Section 17, Table 1 in order for samples to be analyzed and reported.
Replace with:
Blank preparation may be accomplished in three possible ways. A nitrogen cylinder with a regulator, a zero air generator, or a canister filled with nitrogen connected directly to a sample port can be used to achieve a blank analysis. A nitrogen cylinder requires a regulator to control the pressure and flow. Blanks must meet the criteria summarized in Section 17, Table 1 in order for samples to be analyzed and reported.

Page 11, Section 16.3.1 states:
Each analytical run of 10 or fewer samples must include a tune, continuing calibration verification (CCV), control standard, blanks, duplicates, and a check/closing standard.
Replace with:
Each analytical run of 10 or fewer samples must include a tune, continuing calibration verification (CCV), control standard, blanks, duplicates, and a CCV/closing standard.

Page 11, Section 16.3.2 states:
All QC, samples, duplicates, and additional injections must be analyzed within a 24-hour time period from the injection time of the valid CCV for the batch to be considered valid and reportable. For QC criteria, see Section 17, Table 1 and Table 2. Below is the required order of analysis for a valid batch:

- PFTBA Tune
- System Blank
- CCV/Opening Standard
- Control Standard
- Method Blank
- Samples (up to 10)
- Duplicate (one every 10 or fewer samples)
- System Blank
- Check/Closing Standard
- System Blank (Optional)

Replace with:
All QC, samples, duplicates, and additional injections must be analyzed within a 24-hour time period from the injection time of the valid CCV or mid-point in the ICAL for the batch to be considered valid and reportable. For QC criteria, see Section 17, Table 1 and Table 2.
After attaching canisters for analysis, a canister leak test should be performed in the Markes software. Ensure canister valves remain closed during the leak test. If the leak test fails, check connection and repeat and/or move to a different sampling port.

Below is an example of an analytical sequence:

- PFTBA Tune
- Lab air, to flush the system before the System Blank (there are no QC checks for this)
- System Blank
- CCV/Opening Standard or ICAL

- Control Standard
- Method Blank
- Samples (up to 10)
- Duplicate (one every 10 or fewer samples)
- System Blank
- CCV/Closing Standard

Page 11, Section 17.2.1 states:
A single point calibration is performed with each analytical batch by analyzing a midpoint calibration standard concentration that is similar to that used in the most recent linearity study. The response factor of the daily calibration standard is used to quantitate the samples. The batch run will be invalidated for impacted analytes if calibration standard criteria are not met and there is not a valid reason for the deviation, i.e., routine maintenance, retune, etc. If there is enough canister pressure, samples must be re-analyzed after calibration standard criteria are confirmed to be performing appropriately.
Replace with:
Calibration can be achieved using either:

- On Agilent systems only: A single point calibration performed with each analytical batch by analyzing a midpoint calibration standard concentration that is similar to that used in the most recent linearity study. The response factor of the daily calibration standard is used to quantitate the samples.
- A full calibration performed with each analytical batch by analyzing all ICAL points. The full ICAL is used to quantitate the samples.
- On Thermo instruments only: Linking the daily sequence back to the last valid ICAL sequence. The last valid ICAL is used to quantitate the samples.

In all cases: The batch run will be invalidated for impacted analytes if calibration standard criteria are not met and there is not a valid reason for the deviation, i.e., routine maintenance, retune, etc. If there is enough canister pressure, samples must be re-analyzed after calibration standard criteria are confirmed to be performing appropriately.

Page 13, Table 1 states:

CCV/Opening Standard	Analyzed once after the daily tune.	Integration results must be within ± 20% and ± 0.300 minutes of the previous calibration standard response.	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another CCV or prepare new CCV and re-analyze. • If the CCV fails for compound(s) and reanalysis is not possible, may invalidate with NLB management approval. • Re-calibrate if criteria continue to not be met.
Control Standard	Analyzed once after the daily CCV.	Must fall within established control criteria (See Table 2).	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another control standard or prepare new control standard and re-analyze. • If the control standard fails for select compound(s) and the sample cannot be reanalyzed, those compounds are invalidated

			with NLB management approval. Document exceedances accordingly. • Re-establish Control Limits.

Replace with:

Agilent Systems: CCV/Opening Standard	Analyzed after the daily tune.	Integration results must be within ± 20% and ± 0.3 minutes of the previous calibration standard response.	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another CCV or prepare new CCV and re-analyze. • If the CCV fails for compound(s) and reanalysis is not possible, may invalidate with NLB management approval. • Re-calibrate if criteria continue to not be met.
Thermo Systems: CCV/Opening Standard or ICAL mid-point	Analyzed after the daily tune.	Calculated concentrations must be within 80-120% of theoretical and ± 0.3 minutes of expected based off previous ICAL.	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another CCV or prepare new CCV and re-analyze. • Consider a bakeout of the TD-GC-MS or full tune of the MS to restore sensitivity. • Run an ICAL if criteria continue to not be met. • If the CCV/Opening standard or ICAL mid-point fails for compound(s) and reanalysis is not possible, may invalidate with NLB management approval.
Control Standard	Analyzed once after the daily CCV/Opening Standard or ICAL.	Must fall within established control criteria (See Table 2).	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another control standard or prepare new control standard and re-analyze. • If the control standard fails for select compound(s) and the sample cannot be reanalyzed, those compounds are invalidated with NLB management approval. Document exceedances accordingly. • Re-establish Control Limits.

Page 14, Table 1 states:

Check/Closing Standard	Analyzed after 10 or fewer samples and at end of analytical batch.	Integration results must be within ± 20% and ± 0.300 minutes of the CCV response. A CCV and/or a control standard can be used; must be analyzed within 24 hours of first standard.	• 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.
System Blank	Analyzed before CCV/opening standard, before check/closing standard, and after samples with high concentrations due to suspected carryover.	<RL.	• If initial system blank is above RL, additional system blanks can be analyzed to clear the analytical system of possible contamination. See sections 5.1 and 5.2 for interferences and limitations. • If sample results following a system blank with values greater than the RL are at least 10x higher than the blank result, it is documented on the daily QC package, but no additional corrective action is required. • If sample results are less than 10x higher than the blank result, the analysis is repeated if possible or the results for impacted analytes in those samples are invalidated. • The cause of contamination is investigated; the entire batch is re-analyzed if required and if sample is available.

Replace with:

Agilent Systems: CCV/Closing Standard	Analyzed after 10 or fewer samples and at end of analytical batch.	Integration results must be within ± 20% and ± 0.3 minutes of the CCV response. A CCV and/or a control standard can be used; must be analyzed within 24 hours of first standard.	• 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.
Thermo Systems: CCV/Closing Standard	Analyzed after 10 or fewer samples and at end of analytical batch.	Calculated concentrations must be within 80-120% of theoretical and ± 0.3 minutes of expected based off previous ICAL. Must be analyzed within 24 hours of CCV/Opening Standard or ICAL mid-point.	• 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.
System Blank	Analyzed before CCV/opening standard/ICAL, before CCV/closing standard, and after samples with high concentrations due to suspected carryover.	<RL.	• If initial system blank is above RL, additional system blanks can be analyzed to clear the analytical system of possible contamination. See sections 5.1 and 5.2 for interferences and limitations. • If sample results following a system blank with values greater than the RL are at least 10x higher than the blank result, it is documented on the daily QC package, but no additional corrective action is required. • If sample results are less than 10x higher than the blank result, the analysis is repeated if possible or the results for impacted analytes in those samples are invalidated. • The cause of contamination is investigated; the entire batch is re-analyzed if required and if sample is available.

Page 17, Table 3 states:

Calibration Curve	To be established annually at a minimum, when major maintenance or major changes	• Minimum of five upscale calibration points. • Each point ran once. • Linear curve is forced through zero.	• If the calibration curve fails, re-analyze. Prepare new calibration standards if criteria still not met. • If linear calibration continues to fail, stop, and begin corrective actions to determine the cause

	are done or when calibration standard no longer meets criteria.	• Use linear regression with correlation coefficient, R ≥ 0.98 (R^2 > 0.96).	of repeated failures, (specifics include instrument maintenance, mixer/diluter issues, and canister issues).
MDL Verification	To be established annually when major maintenance or major changes are done.	• The MDL must be below RL. • Minimum of seven replicates are required. • The seven replicates may be achieved with one canister. • Must meet window criteria of MDL < Spike Concentration < 10x MDL.	• If the MDL is not below RL, the MDL Verification fails and must be evaluated and possibly re-analyzed. • If the MDL is below the RL and does not meet the window criteria, the MDL must be attempted again at a lower spike concentration unless it was performed at the lowest feasible concentration. • If the re-analyzed MDL is below the RL, and still does not meet the window criteria, the MDL may be accepted with management approval. Document what was attempted.

Replace with:

Initial Calibration (ICAL)	To be established annually at a minimum, when major maintenance or major changes are done or when calibration standard no longer meets criteria.	• Minimum of five (Agilent) or six (Thermo) calibration points. • Agilent systems: Use linear regression, no weighting, forced through zero. Pass criteria, R ≥ 0.98 (R^2 > 0.96). • Thermo systems: Use quadratic fit, 1/amount^2 weighting, with offset. Pass criteria, R^2 > 0.96.	• If the calibration curve fails, re-analyze. Prepare new calibration standards if criteria still not met. • If calibration continues to fail, stop, and begin corrective actions to determine the cause of repeated failures, (specifics include instrument maintenance, mixer/diluter issues, and canister issues).
MDL Verification	To be established annually when major maintenance or major changes are done.	• Minimum of seven replicates are required. • The seven replicates may be achieved with one canister. • Recovery within 50-150% • Must meet window criteria of MDL < Spike Concentration < 10x MDL.	• If the MDL criteria is not met, then re-analyze using a preparation of another MDL spike, if feasible. • If the MDL criteria is still not met, the MDL may be accepted with justification and management approval. This must be documented and placed in the MDL data package.

Page 18, Section 18.4 states:
The Percent Difference calculation for opening and closing standard criteria is as follows:

$$\% \text{ Difference} = \frac{Area_{New\ Standard} - Area_{Old\ Standard}}{Area_{New\ Standard}}\ x\ 100\%$$

Replace with:

The Percent Difference calculation for opening and closing standard criteria (Agilent systems only) is as follows:

$$\% \text{ Difference} = \frac{Area_{New\ Standard} - Area_{Old\ Standard}}{Area_{New\ Standard}}\ x\ 100\%$$

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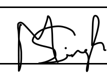
Section 5. Justification for Deviation(s) *(provide explanation of why modification(s) to existing ARB document is necessary)*
The changes above reflect: • Continued method optimization on the Thermo GC-MS systems since the first draft was prepared.

Section 6. Attachment(s) ☐ *(specify attachment titles and number of pages, include modified spreadsheets or forms)*	**# of Pages**

Section 7. ARB Approval *(completed by ARB)*		
Name/Phone Number:	Manisha Singh, Ph.D.	279-208-7896
Title:	Chief, Quality Management Branch	
Signature/Date:		6/13/2024
Addendum Number	A48	

Completed form must be scanned/emailed or mailed to: Manisha Singh, Ph.D. 1927 13th Street, P.O. Box 2815 Sacramento, California 95811 manisha.singh@arb.ca.gov

State of California
California Environmental Protection Agency
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MLD/QMS-066 (NEW 4/14)

QUALITY MANAGEMENT DOCUMENT ADDENDUM

(District completes Sections 1 through 6 -- please type)

Section 1. ARB Document
☐ Quality Management Plan (QMP)
☐ Quality Assurance Project Plan (QAPP)
☒ Standard Operating Procedure (SOP)

Section 2. District Information		
Agency Name:	Northern Laboratory Branch Monitoring and Laboratory Division	
Agency Address:	1927 13th Street, Sacramento	
Prepared by:	David Wevill, Air Pollution Specialist, Dec 8 2021	
Agency Contact Name/Phone Number:	Patrick Rainey	(916) 327-4756
Agency Signature/Date:	Patrick Rainey	1/12/2022

Section 3. Document Title *(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)*	**Date**
STANDARD OPERATING PROCEDURE FOR ANALYSIS OF VOLATILE ORGANIC AND OXYGENATE COMPOUNDS IN AMBIENT AIR USING GAS CHROMATOGRAPH/MASS SPECTROMETER MLD072 Revision 0.0	May 14 2021

Section 4. Proposed Deviation(s) (specify exact section(s), page number(s) and language in existing ARB document that your District proposes to modify and then specify proposed modification (including any spreadsheets or forms).
Page 6, Section 9.2 states: Column, such as DB-624, 60 m, 0.32 mm id, 1.4 µm thickness, or equivalent (part# 123-1364). **Replace with:** Column, capable of achieving the performance criteria defined in section 17. Examples include 1% phenol or ‘volatile’ columns with a typical 60 m length, 0.32 mm I.D., and 1.00 µm or greater film thickness. **Page 6, Section 9.10 states:** Liquid nitrogen **Remove this section (refers to obsolete equipment)**

Page 9, Section 15.4 states: Grab samples, which are collected without a pump or calibrated orifice, may arrive with zero psig. These samples require pressurization with UHP nitrogen gas prior to sample analysis. A dilution factor (DF) is applied to the final data results in LIMS. See the gaseous mixer/diluter SOP MLD074 for details on pressurizing grab samples.

Replace with: Grab samples, which are collected without a pump or calibrated orifice, may arrive with zero psig. If using a concentrator capable of sampling from sub-ambient pressure canisters (such as the Markes system described in Section 9) then no dilution is necessary, otherwise these samples require pressurization with UHP nitrogen prior to sample analysis. If diluted then a dilution factor (DF) is applied to the final data results in LIMS. See the gaseous mixer/diluter SOP MLD074 for details on pressurizing grab samples.

Page 10, Section 16.2.1 states: Sample canisters are connected to the instrument using Teflon tubing attached to the canisters by 9/16-inch fittings.

Replace with: Sample canisters are connected to the instrument using Teflon, stainless steel or inert coated stainless steel tubing attached to the canisters by 9/16-inch fittings.

Page 21, sections 22.3 and 22.4 state:

22.3. Saturn 2000 GC/MS, Hardware Operation Manual, Agilent, 2007. http://www.ecs.umass.edu/eve/facilities/equipment/Varian2200/914978.pdf

22.4. Saturn 2000 GC/MS, MS Workstation, Operation Manual, Agilent, May 2010. https://www.agilent.com/cs/library/usermanuals/public/914979.pdf

Remove these sections (refers to obsolete equipment)

Page 22, Appendix 1 states:

OLS-MLD072-A1

Typical Thermal Desorption Methods for MLD072

Note – These operating conditions are specific to CARB's use of Markes units with a Thermo or Agilent GC/MS. This section also covers the sample delivery system for the Saturn GCMS. Method parameters may change if needed by an experienced analyst and by management approval.

Markes units with a Thermo or Agilent GC/MS

Standby – Split On; 30 mL/min
Leak Test – On
Flow Path – 160oC
GC Cycle Time – 53 minutes
Minimum Carrier Pressure – 1 psi

Pre-Sampling Tab:
Sample Purge Time – 2.0 minutes at 50 mL/min
Kori Trap Low – -30oC
Kori Trap High – 300oC

Sampling Tab:
Sample by Volume – Yes
Sample Quantity – 300 mL/min
Post Sampling Purge Time – 5 minutes at 50 mL/min

Post-Sampling Tab:

Trap Purge – 3 minutes at 50 mL/min
Trap Low – 30oC
Trap High – 240oC
Trap Heating Rate (oC/s) – MAX
Trap Hold – 1 minute; split on; 20 mL/min

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

Kori-xr Trap Purge Flow – approx. 100 mL/min
Load Volume: 300 mL
Replace with:
OLS-MLD072-A1

Typical Thermal Desorption Methods for MLD072

Note – These operating conditions are specific to CARB's use of Markes units with a Thermo or Agilent GC/MS. Method parameters may change if needed by an experienced analyst and by management approval.

Markes units with an Agilent GC/MS

Standby – Split On; 30 mL/min
Leak Test – On
Flow Path – 160oC
GC Cycle Time – 53 minutes
Minimum Carrier Pressure – 1 psi

Pre-Sampling Tab:
Sample Purge Time – 2.0 minutes at 50 mL/min
Kori Trap Low – -30oC
Kori Trap High – 300oC

Sampling Tab:
Sample by Volume – Yes
Sample Quantity – 300 mL/min
Post Sampling Purge Time – 5 minutes at 50 mL/min

Post-Sampling Tab:
Trap Purge – 3 minutes at 50 mL/min
Trap Low – 30oC
Trap High – 240oC
Trap Heating Rate (oC/s) – MAX
Trap Hold – 1 minute; split on; 20 mL/min

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

Kori-xr Trap Purge Flow – approx. 100 mL/min
Load Volume: 300 mL

Markes units with a Thermo GC/MS

Standby – Split On; 10 mL/min
Leak Test – On
Flow Path – 100oC
GC Cycle Time – 18 minutes
Minimum Carrier Pressure – 1 psi

Pre-Sampling Tab:
Sample Purge Time – 2.0 minutes at 75 mL/min
Kori Trap Low – -30oC
Kori Trap High – 300oC

Sampling Tab:
Sample by Volume – Yes
Sample Quantity – 500 mL/min
Post Sampling Purge Time – 3 minutes at 75 mL/min

Post-Sampling Tab:
Trap Purge – 1 minutes at 50 mL/min
Trap Low – -30oC
Trap High – 250oC
Trap Heating Rate (oC/s) – 40
Trap Hold – 8 minute; split on; 10 mL/min

Helium CIA Pressure – approx. 25 psi
Nitrogen Pneumatics – approx. 55 psi

Kori-xr Trap Purge Flow – approx. 100 mL/min
Load Volume: 500 mL

Page 23, Appendix 1 states:
Sample Delivery System Temperature Zones for a Varian Saturn GCMS
Zone 1: Front Injector 1079 (carbon trap)

Rate (ºC/min)	Target Value (ºC)	Hold Time (minutes)	Run Time (minutes)
0.00	145.0	9.00	9.00
200.0	275.0	52.35	62.00

Zone 2: Middle Injector 1079 (cryofocuser)

Rate (ºC/min)	Target Value (ºC)	Hold Time (minutes)	Run Time (minutes)
0.00	200.0	2.00	2.00
200.0	-30.0	9.85	13.00
200.0	250.0	47.60	62.00

Zone 3: Middle Valve – (sample lines)

Rate (mL/min/min)	**Flow (mL/min)**	**Hold Time (minutes)**	**Run Time (minutes)**
0.00	1.60	52.00	52.00
2.00	2.00	9.80	62.00

Zone 4: Front FID- Not used

Zone 5: Middle FID - valve oven with SSV 80C

Zone 6: Front Valve - 2 valve oven 150C

Helium Output Pressure – approx. 80 psi
Nitrogen Output Pressure – approx. 60 psi
Liquid Nitrogen Dewar Pressure Range – approx. 35-50psi
Load Volume: 150 mL
Remove the above from the section (refers to obsolete equipment)

Page 24, Appendix 2 states:
OLS-MLD072-A2

Typical GC/MS Methods for MLD072

Note – these operating conditions are specific to CARB's use of an Agilent, Thermo, or Saturn GC/MS. Method parameters may change if needed by an experienced analyst and by management approval.

Thermo GC Parameters:
Front Inlet – 200oC
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 – Off
Front Inlet Flow – 1.200 mL/min
GC Standby Temp – 100oC

Thermo Column Oven Parameters:

Retention Time (minutes)	Rate (^{o}C/min)	Target Value (^{o}C)	Hold Time (minutes)
5.00	0.00	35.0	5.00
33.0	5.00	170.0	1.00
39.25	40.00	220.0	5.0

Thermo MS Parameters:
Ion Source (Thermo MS) – 330oC
MS Transfer Line – 230oC
Ionization Mode – EI

Segment	Time (minutes)	Range (amu)	Dwell/Scan Time (seconds)	Total Scan (seconds)	Filament On	Detector Gain
1	4.25	47-200	0.15	0.154	YES	3.00×10^5
2	5.00	50, 53, 54, 62, 64	0.15, 0.15, 0.15, 0.15, 0.15	0.9244	YES	3.00×10^5
-----	-----	47-200	0.15	0.154	YES	3.00×10^5
3	6.00	47-200	0.15	0.154	YES	3.00×10^5
4	8.00	42, 43, 44, 45, 46	0.15, 0.15, 0.15, 0.15, 0.15	0.9244	YES	3.00×10^5
-----	-----	35-200	0.15	0.154	YES	3.00×10^5
5	8.85	35-200	0.15	0.154	YES	3.00×10^5
6	27.00	35-200	0.15	0.154	NO	3.00×10^5

Agilent GC Parameters:

Front Inlet – 40°C

Front Inlet Pressure Mode – On

Front Inlet Pressure Control – 15 psi

Total Flow – 102.89 mL/min

Purge Flow to Split Vent – 100 mL/min at 999.99 minutes

Front Inlet Split Mode – Splitless

Initial Flow at Beginning of Run – 2.393 mL/min at 35°C

GC Standby Temp – 100°C

Agilent Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	35.0	5.00	5.00
5.00	135.0	1.00	26.00
40.00	220.0	4.875	33.00

Agilent MS Parameters:

Ion Trap (Agilent MS) – 150°C

MS Transfer Line – 170°C

Ionization Mode – Internal EI

Mass Data Type – Centroid

Target TIC – 30000 counts

Max Ion Time – 35000 µSeconds

Emission Current – 40 µAmps

Scan Type – Full

Number of Segments – 4

Scan Speed – Normal

Offset – 100

Segment	Time (minutes)	Range (amu)	Low Mass (m/z)	High Mass (m/z)	Storage Level (m/z)	Ion Time Factor (%)	Filament On
1	0-3.00	none	10	99	35	35	OFF
2	3.00-5.26	49-190	100	249	35	35	ON
3	5.26-26.00	35-190	250	399	35	35	ON
4	26.00-33.00	none	400	1000	35	35	OFF

Replace with:
OLS-MLD072-A2

Typical GC/MS Methods for MLD072

Note – these operating conditions are specific to CARB's use of an Agilent or Thermo GC/MS. Method parameters may change if needed by an experienced analyst and by management approval.

Thermo GC Parameters:
Front Inlet – 120oC
Front Inlet Flow Mode – FlowCtrl
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 – Off
Front Inlet Flow – 3.000 mL/min

Thermo Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Retention Time (minutes)
0.00	35	4.5	4.5
8.00	70	0.0	8.9
20.00	95	0.0	10.13
35.00	225	3.0	16.84

Thermo MS Parameters:

Ion Source (Thermo MS) – 310°C

MS Transfer Line – 230°C

Ionization Mode – EI

Segment	Time (minutes)	Range (amu)	Dwell Time (seconds) / SIM width (amu)
1	1.00	39,41,43,45,46,49,51,52,53,54,55,56,58,61,62,84,85,87,94,96,101, 103,105	0.01 / 0.50
-----	-----	35-200	0.15
2	3.20	51,52,53,75,83,97,117,130	0.01 / 0.50
-----	-----	42-200	0.10
3	8.80	42-300	0.10

Agilent GC Parameters:

Front Inlet – 40oC
Front Inlet Pressure Mode – On
Front Inlet Pressure Control – 15 psi
Total Flow – 102.89 mL/min
Purge Flow to Split Vent – 100 mL/min at 999.99 minutes
Front Inlet Split Mode – Splitless
Initial Flow at Beginning of Run – 2.393 mL/min at 35oC
GC Standby Temp – 100oC

Agilent Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	35.0	5.00	5.00
5.00	135.0	1.00	26.00
40.00	220.0	4.875	33.00

Agilent MS Parameters:

Ion Trap (Agilent MS) – 150oC
MS Transfer Line – 170oC
Ionization Mode – Internal EI
Mass Data Type – Centroid
Target TIC – 30000 counts
Max Ion Time – 35000 µSeconds
Emission Current – 40 µAmps
Scan Type – Full
Number of Segments – 4
Scan Speed – Normal

Offset – 100

Segment	Time (minutes)	Range (amu)	Low Mass (m/z)	High Mass (m/z)	Storage Level (m/z)	Ion Time Factor (%)	Filament On
1	0-3.00	none	10	99	35	35	OFF
2	3.00-5.26	49-190	100	249	35	35	ON
3	5.26-26.00	35-190	250	399	35	35	ON
4	26.00-33.00	none	400	1000	35	35	OFF

Page 26, Appendix 2 states:

Saturn 3800 GC Parameters:
Front Inlet – 50oC
Front Inlet Pressure Mode – On
Front Inlet Pressure – 12 psi
Linear Velocity – 40.5 cm/sec
Initial Flow at Beginning of Run – 1.6 mL/min at 100oC
GC Standby Temp – 100oC
Coolant Timeout – 60min
Coolant Used – Liquid Nitrogen

Saturn 3800 Column Oven Parameters:

Rate (oC/min)	Target Value (oC)	Hold Time (minutes)	Run Time (minutes)
0.00	100.0	8.20	8.20
100.0	-20.0	3.60	13.00
4.00	140.0	0.00	53.00
100.0	200.0	8.40	62.00

Saturn 2000 MS Parameters:
Ion Trap (Saturn MS) – 150oC
MS Transfer Line – 170oC
Manifold – 50oC
Ionization Mode – EI AGC
Mass Data Type – Centroid
Target TIC – 20000 counts
Max Ion Time – 25000 µSeconds
Background mass – 33m/z
RF Dump Value – 650m/z
Emission Current – 30 µAmps
Scan Type – Full
Number of Segments – 2
Scan Speed – Normal
Offset – none

Segment Start Time (minutes) End
Time (minutes) Range (amu) Low Mass (m/z) High Mass (m/z) Storage Level (m/z) Ion
Time Factor (%) Filament On
1 0.00 4.00 10-99 40 650 32 100 NO
2 4.00 49.00 100-249 33 200 32 100 YES

Remove this section (refers to obsolete equipment)

Page 27, Appendix 3 states:

OLS-MLD072-A3
Target Compounds Validated by MLD072

Compounds	RL (PPB)	CAS Number
Dichlorodifluoromethane (Freon 12)	0.020	75-71-8
Vinyl Chloride	0.020	75-01-4
1,3-Butadiene	0.040	106-99-0
Bromomethane	0.030	74-83-9
Trichlorofluoromethane (Freon 11)	0.010	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	0.020	76-13-1
Dichloromethane	0.100	75-09-2
Chloroform	0.020	67-66-3
Methyl Chloroform	0.010	71-55-6
Carbon Tetrachloride	0.020	56-23-5
Benzene	0.050	71-43-2
Trichloroethylene	0.020	79-01-6
cis-1,3-Dichloropropene	0.100	10061-01-5
Toluene	0.200	108-88-3
trans-1,3-Dichloropropene	0.100	10061-02-6
Tetrachloroethylene	0.010	127-18-4
Ethylbenzene	0.200	100-41-4
m/p-Xylene	0.200	108-38-3 106-42-3
o-Xylene	0.100	95-47-6
Styrene	0.100	100-42-5
Acrolein	0.300	107-02-8
Acetone	1.000	67-64-1
Acetonitrile	0.300	75-05-8
Acrylonitrile	0.300	107-13-1

Replace with:

OLS-MLD072-A3
Target Compounds Validated by MLD072

Compounds	RL (PPB)	CAS Number
Dichlorodifluoromethane (Freon 12)	0.020	75-71-8
Vinyl chloride	0.020	75-01-4
1,3-Butadiene	0.040	106-99-0
Bromomethane	0.030	74-83-9
Trichlorofluoromethane (Freon 11)	0.010	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	0.020	76-13-1
Dichloromethane	0.100	75-09-2
Chloroform	0.020	67-66-3
1,1,1-Trichloroethane	0.010	71-55-6
Carbon tetrachloride	0.020	56-23-5
Benzene	0.050	71-43-2
Trichloroethylene	0.020	79-01-6

cis-1,3-Dichloropropene	0.100	10061-01-5
Toluene	0.200	108-88-3
trans-1,3-Dichloropropene	0.100	10061-02-6
Tetrachloroethylene (Perchloroethylene)	0.010	127-18-4
Ethylbenzene	0.200	100-41-4
m/p-Xylene	0.200	108-38-3 106-42-3
o-Xylene	0.100	95-47-6
Styrene	0.100	100-42-5
Acrolein	0.300	107-02-8
Acetone	1.000	67-64-1
Acetonitrile	0.300	75-05-8
Acrylonitrile	0.300	107-13-1

Page 28, Appendix 4 states:

OLS-MLD072-A4
Example Calibration Levels for VOCs
Mid-Point 2.000 PPB

LEVELS OF CONCENTRATION (PPB)								
DF	1/10000	1/3220	1/970	1/324	1/100	1/50	1/30	1/20
PPB	0.010	0.031	0.103	0.309	1.000	2.000	3.330	5.000

Example Calibration Levels for Oxygenates
Mid-Point at DF 0.02

DF	Acrolein (PPB)	Acetone (PPB)	Acetonitrile (PPB)	Acrylonitrile (PPB)
0.0004	0.100	0.370	0.0925	0.0929
0.0008	0.200	0.740	0.185	0.186
0.0025	0.600	2.220	0.555	0.558
0.0067	1.600	5.920	1.480	1.487
0.013	3.200	11.840	2.960	2.973
0.02	4.800	17.760	4.440	4.460
0.033	8.000	29.660	7.400	7.433
0.05	12.000	44.400	11.100	11.150

Replace with:

OLS-MLD072-A4
Example Calibration Levels for VOCs
Mid-Point 2.000 PPB

LEVELS OF CONCENTRATION (PPB)								
DF	1/10000	1/3220	1/970	1/324	1/100	1/50	1/30	1/20
PPB	0.010	0.031	0.103	0.309	1.000	2.000	3.330	5.000

Note: Concentrations may vary but calibration levels should include a lower level at or below the RL for each analyte

Example Calibration Levels for Oxygenates
Mid-Point at DF 1/50

DF	Acrolein (PPB)	Acetone (PPB)	Acetonitrile (PPB)	Acrylonitrile (PPB)
1/2500	0.096	0.355	0.089	0.089
1/1250	0.192	0.710	0.178	0.178
1/400	0.600	2.220	0.555	0.558
1/150	1.600	5.920	1.480	1.487
1/77	3.117	11.532	2.883	2.896
1/50	4.800	17.760	4.440	4.460
1/30	8.000	29.600	7.400	7.433
1/20	12.00	44.40	11.10	11.15

Note: Concentrations may vary but calibration levels should include a lower level at or below the RL for each analyte

Section 5. Justification for Deviation(s) *(provide explanation of why modification(s) to existing ARB document is necessary)*
The changes above reflect: • The obsoletion of old equipment (Varian Saturn 2000 GC-MS) • Continued method optimization on the Thermo GC-MS systems since the first draft was prepared • Clarification and correction of some minor points

Section 6. Attachment(s) ☐ *(specify attachment titles and number of pages, include modified spreadsheets or forms)*	**# of Pages**

Section 7. ARB Approval *(completed by ARB)*		
Name/Phone Number:	Manisha Singh	(279) 208-7896
Title:	Chief, Quality Management Branch	
Signature/Date:	M Singh	1/31/2022
Addendum Number	A36	

Completed form must be scanned/emailed or mailed to:

Quality Management Section
1927 13th Street, P.O. Box 2815
Sacramento, California 95811
greg.gilani@arb.ca.gov

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF VOLATILE ORGANIC AND OXYGENATE COMPOUNDS IN AMBIENT AIR USING GAS CHROMATOGRAPH/MASS SPECTROMETER

MLD072
Revision 0.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph.D., Chief Quality Management Branch	March 1, 2021
Michael Werst, Chief Northern Laboratory Branch	May 14, 2021

Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the California Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the California Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF VOLATILE ORGANIC AND OXYGENATE COMPOUNDS IN AMBIENT AIR USING GAS CHROMATOGRAPH/MASS SPECTROMETER

1. SCOPE

This method describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze volatile organic compounds (VOCs) and oxygenates in ambient air samples using a gas chromatograph/mass spectrometer (GC/MS). See Appendix 3 for a list of compounds that have been validated for this method. This method is a replacement for the existing methods MLD058 VOCs and MLD066 oxygenates which can be used for any or all of the target compounds in either of those methods. 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 stainless steel canisters at monitoring stations located throughout California. Canisters are filled using a pump such as a Xonteck 910 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
inHg	Inches of Mercury
AMU	Atomic Mass Units
CAS	Chemical Abstract Service
CCV	Continuing Calibration Verification
DF	Dilution Factor
GC/MS	Gas Chromatograph/Mass Spectrometer
LIMS	Laboratory Information Management System

LOQ	Limit of Quantitation
M/Z	mass-to-charge ratio
MDL	Method Detection Limit
MLD	Monitoring and Laboratory Division
MSD	Mass Spectral Detector
Acronym or Term	**Definition**
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
OLS	Organics Laboratory Section
PFTBA	Perfluorotributylamine
PPB	Parts per Billion
PSIA	Pounds per Square Inch Absolute
PSIG	Pounds per Square Inch Gauge
QC	Quality Control
QCM	Quality Control Manual
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
UHP	Ultra High Purity
VOC	Volatile Organic Compounds

4. DEFINITIONS

4.1. ANALYTICAL BATCH – A set of samples analyzed together as a group in an uninterrupted sequence.

4.2. 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 response for the target compounds.

4.3. 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. (See Continuing Calibration Verification).

4.4. CARRYOVER – Contamination from an adjacent sample causing false or inaccurate results in the subsequent sample(s).

4.5. CARRYOVER CHECK – The high-level sample is re-analyzed followed by a blank to determine if any possible carryover may have occurred that would cause inaccurate results in the subsequent sample(s).

4.6. CHECK / CLOSING STANDARD – A mid-level standard containing the target analytes at a known concentration analyzed at the end of every batch after sample analysis to confirm stability of the instrument. (See Continuing Calibration Verification).

4.7. COLLOCATED SAMPLE – A sample used to assess total precision (sampling and analysis) collected within a specified radius of the primary sample. The collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.

4.8. CONTINUING CALIBRATION VERIFICATION (CCV) / OPENING CALIBRATION – A calibration 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. If a second source is not available, the standard may be prepared by a different person or on a different day. The mid-level calibration standard is analyzed in a GC/MS system that has met the tuning and mass calibration criteria. (See Calibration Standard).

4.9. CONTROL STANDARD – A standard containing the target analytes at a known concentration obtained from a source other than that of the calibration standard (primary source) or from a different lot number. If a second source is not available, the standard may be prepared by a different person or on a different day. This control contains all target compounds and is used to maintain quality control (QC) charts.

4.10. DILUTION – Is the process of reducing the concentration of a solute in solution. Dilutions are required when any sample concentration exceeds the calibrated linear range by more than ten percent. After diluting, the concentration should fall within the calibrated linear range.

4.11. DUPLICATE – A re-analysis of a sample within an analytical batch that is processed through the entire analytical method to show precision.

4.12. HOLD TIME – The maximum amount of time a sample may be stored prior to performing an operation. Analytical hold time for canister analysis is from sample collection to analysis.

4.13. INTERFERENCE – Discrete artifacts or elevated baselines from environmental factors that may cause systematic errors in measurement of the sample being analyzed or misinterpretation of the chromatographic data.

4.14. LIMIT OF QUANTITATION (LOQ) – 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 analysis from the method detection limit (MDL) determination/verification. LOQ is analyte and instrument specific.

4.15. METHOD DETECTION LIMIT (MDL) – A statistically derived value that is defined as being the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sample media) containing the analytes of interest.

4.16. REPORTING LIMIT (RL) – 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.

4.17. SPIKE – A quality control sample employed to evaluate the accuracy of a measurement. A spike is prepared by adding a known amount of the target analyte(s) to an aliquot of the sample or to media prior to sampling. The recovery of a spike provides an indication of the efficiency of the analytical procedure for a given matrix. Spikes can be designated as field, laboratory, matrix, and trip spikes. Field spikes are used to assess matrix interferences.

4.18. SYSTEM / METHOD BLANK – An aliquot of nitrogen gas analyzed and used to monitor the laboratory analytical systems for interferences and contamination.

5. INTERFERENCES AND LIMITATIONS

5.1. 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 (m/z) ratio as the target compound. This can lead to misidentification or inaccurate quantitation.

5.2. 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 blanks should be analyzed and verified to have results below the reporting limit (RL) prior to reanalyzing the succeeding sample(s).

5.3. High boiling point compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column must be baked out to remove these contaminants prior to analyzing samples if present. The bake out temperature must not exceed the column’s maximum operating temperature.

5.4. Although studies have shown that the target compounds can be considered stable in stainless steel canisters, every effort must be made to analyze the sample as soon as possible. Care must be taken to prevent contamination during sample collection, transportation, and subsequent analysis.

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, staff with expert knowledge of this method must train new personnel. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel must also be trained to safely and properly operate the equipment needed to perform the method, the quality assurance components, and Laboratory Information Management System (LIMS) functionality pertaining to the program. Personnel must provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record). Training will be documented and maintained by the laboratory supervisor.

7. SAFETY REQUIREMENTS

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

7.1. The analyst must wear protective eyewear, lab coat, and nitrile gloves whenever working with liquid standards, solvents, and solutions. Solvents are very flammable; standards are irritants, particularly to the eyes and skin, and possibly very toxic. Refer to the safety data sheet (SDS) for specifics regarding handling, as well as emergency procedures.

7.2. 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.

7.3. The GC and MS have heated zones (refer to applicable instrument manual for specifics), which may cause burns. The cold 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.

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. Gas chromatograph with a programmable oven, electronic pressure control for capillary columns, heated injector, and analog pressure gauges for gas monitoring.

9.2. Column, such as DB-624, 60 m, 0.32 mm id, 1.4 μm thickness, or equivalent (part# 123-1364).

9.3. Detector: mass spectral detector (MSD).

9.4. Software: A data station for control of GC, MS plus storage and quantification of mass spectral data. (See References Section 22 for details).

9.5. Adsorbent cold trap, such as a Markes TO-15 cold trap or equivalent.

9.6. Stainless steel passivated SUMMA canisters - size 6 liters. Vacuum source (house or local vacuum pump).

9.7. Multi-canister auto-sampler equipped with mass flow controllers to allow for loading variable sample volumes such as a Markes CIA Advantage or equivalent.

9.8. Sample concentrator, such as a cryofocuser or a Markes Unity 2 or equivalent.

9.9. Water management control, such as a cryofocuser or a Markes Kori-xr or equivalent.

9.10. Liquid nitrogen

9.11. Syringes, such as 250 μL and 250mL.

9.12. Reagent grade water purification system, such as Elga Labwater model No. PURELAB Flex 2, or equivalent.

9.13. Flow controlled gaseous mixer/diluter, Environics model 2040, or equivalent.

10. REAGENTS AND GASES

Consult the latest version of the Quality Control Manual (QCM) for the calibration gas requirements.

10.1. Perfluorotributylamine (PFTBA) or MS tune solution.

10.2. Ultra High Purity (UHP) Helium, 99.999% for use as the GC column carrier gas.

10.3. UHP Nitrogen, 99.999% for use as the make-up gas.

10.4. A calibration and control standard gas cylinder, containing the analytes of interest.

11. STANDARDS PREPARATION

11.1. Gaseous standards are in a high-pressure cylinder with known certified concentrations. Cylinder standards are stable and are valid through the manufacturer’s expiration date.

11.2. Preparing a Gaseous Standard

11.2.1. Gaseous standards are prepared with a flow-controlled gaseous mixer/diluter. For each gaseous standard canister prepared, spike the single 6 L canister with 150 µL of reagent grade water. With the canister connected to the gaseous mixer/diluter, set the diluter to the appropriate dilution setting for the gas standard, open the canister to begin filling with the desired gaseous concentration until pressurized to 25 psig. Refer to SOP MLD074 for detailed instructions on operating the diluter. Allow canister to equilibrate overnight before use. Working standards are typically assigned a 60 day expiration date from preparation, but not to exceed the expiration date of the neat standard.

11.2.2. When available, certified calibration gas standards are purchased from National Institute of Standards and Technology (NIST). Calibration and control standards may be purchased from other approved vendors provided they are NIST traceable. The standards used are NIST traceable by either a weight process utilizing NIST calibrated scales and/or using reference materials from a nationally recognized institute (such as NIST) to calibrate the analytical measurement system used to verify the concentration of the mixture components. The Certificate of Analysis (see Appendix 5) shall reflect the actual analysis of the specific cylinder shipped to customer, as evidenced by cylinder number. The analytical uncertainty of each cylinder must be less than +/-10% of the actual concentration.

11.2.3. 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. (See Appendix 4 for example concentrations).

12. FIELD SPIKES

These spikes are prepared in the laboratory at client request only and are sampled and analyzed with the un-spiked collocated sample. With the spiked and un-spiked sample, a percent recovery can be determined. The data obtained from these spikes can serve as an indication of matrix interferences.

12.1. All canisters used must be evacuated to 29.5 inches of mercury (inHg) or greater. Prior to using the canister, verify vacuum with a calibrated gauge.

12.2. Using a clean syringe, inject the canister with 50 µL of reagent grade water.

12.3. Using a 250 mL gas tight syringe, take an aliquot of the gaseous standard and inject it into the canister. The spike volume may range from 50 mL to 200 mL of standard, depending on the project.

12.4. Check and record the vacuum of the canister after the standard is injected.

12.5. The canisters are sent out to the field for sampling in the same manner as the un-spiked canister.

12.6. The spiked and un-spiked canisters are analyzed on a GC/MS in the same manner as any other sample.

12.7. Spike samples are required to have the Relative Percent Difference (RPD) evaluated and the criteria can be found in Section 17, Table 2 of this SOP.

13. SAMPLE STORAGE AND HOLD TIME

13.1. All samples are stored at room temperature until analysis.

13.2. Samples must be analyzed within 30 days of sample collection.

13.3. After sample analysis, samples are stored until completion of all applicable methods.

14. BLANK PREPARATION

Blank preparation may be accomplished in two possible ways. A nitrogen cylinder with a regulator or canister filled with nitrogen connected directly to a sample port can be used to achieve a blank analysis. A nitrogen cylinder requires a regulator to control the pressure and flow. Either of these types of blanks must meet the criteria summarized in Section 17, Table 1 in order for samples to be analyzed and reported.

To use a blank from a stainless-steel canister, it must be prepared as follows:

14.1. Stainless steel canister must be clean, free of any target compounds and have a vacuum of 29.5 inHg or greater.

14.2. Allow the mixer/diluter to condition and purge the lines with UHP nitrogen for at least 30 minutes before use.

14.3. Inject 150 µL of reagent grade water into the canister.

14.4. Pressurize canister to 25 psig.

15. SAMPLE PREPARATION

15.1. Samples in canisters must be equilibrated at laboratory room temperature overnight prior to analysis.

15.2. Samples taken for analysis are to be signed out from the Toxics Login Sheet Binder, which is used to track the analyses completed for each sample.

15.3. Sample canister pressures must be at least 5 psig when received from the field unless it is a grab sample. If pressure is less than 5 psig, the sample is invalid unless it is a grab (non-flow-controlled) sample. If the pressure is over 16 psig, it should be documented, but the sample is still valid. (A 24-hour sample with a pressure >16psig may be indicative of inconsistent sampling).

15.4. Grab samples, which are collected without a pump or calibrated orifice, may arrive with zero psig. These samples require pressurization with UHP nitrogen gas prior to sample analysis. A dilution factor (DF) is applied to the final data results in LIMS. See the gaseous mixer/diluter SOP MLD074 for details on pressurizing grab samples.

15.5. After connecting analytical sample lines to canisters, confirm leak tight connections by running a canister leak test with the instrument software.

15.6. Create a sample/sequence list on the workstation computer for the samples to be analyzed.

16. ANALYSIS

16.1. Instrument Performance Check

16.1.1. 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.

16.1.2. The tune value, with regard to positions and abundance ratios of the tune m/z and their corresponding isotope m/z's, must be reviewed. Refer to applicable manual for specific criteria.

16.1.3. The system must be checked for leaks and the electron multiplier voltage must be checked and evaluated. Corrective action must be performed if needed prior to analyzing samples. Refer to applicable manual for specific criteria.

16.1.4. The tuning report must be saved and archived with associated sample data.

16.1.5. Verify all QC described in Section 17, Table 1 has been met prior to analyzing samples.

16.2. Sample Concentration and Analysis

16.2.1. Sample canisters are connected to the instrument using Teflon tubing attached to the canisters by 9/16-inch fittings.

16.2.2. Samples are introduced onto the sorbent trap under control of the thermal desorption equipment and method. These parameters are described in the Appendix OLS-MLD072-A1.

16.2.3. 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 OLS-MLD072-A2.

16.2.4. The ambient samples are analyzed using the same sample volume as used for the calibration and control standards. If a target analyte concentration exceeds the upper linear range by more than ten percent, a dilution is required, which can be accomplished by an injection of a smaller volume. The final concentration is calculated by multiplying the dilution analysis concentration by the DF.

16.3. Analytical Sequence

16.3.1. Each analytical run of 10 or fewer samples must include a tune, continuing calibration verification (CCV), control standard, blanks, duplicates, and a check/closing standard.

16.3.2. All QC, samples, duplicates, and additional injections must be analyzed within a 24-hour time period from the injection time of the valid CCV for the batch to be considered valid and reportable. For QC criteria, see Section 17, Table 1 and Table 2. Below is the required order of analysis for a valid batch:

- PFTBA Tune
- System Blank
- CCV/Opening Standard
- Control Standard
- Method Blank
- Samples (up to 10)
- Duplicate (one every 10 or fewer samples)
- System Blank
- Check/Closing Standard
- System Blank (Optional)

16.4. Instrument Method

A typical method is shown in the Appendix, OLS-MLD072-A1 and OLS-MLD072-A2. A list of compounds and RLs are shown in Appendix, OLS-MLD072-A3.

17. QUALITY CONTROL

17.1. Several types of QC samples are evaluated daily, annually, or as needed to verify the instrument is still under control and meet the required acceptance criteria. These are described in Tables 1, 2, and 3 below. If QC results are not met, corrective action(s) must be taken. Occasionally, deviations may be necessary which shall require documentation and management approval prior to use. These deviations must be documented on the data review checklist in the daily batch packet and on the final monthly QC report.

17.2. Continuing Calibration Verification

17.2.1. A single point calibration is performed with each analytical batch by analyzing a midpoint calibration standard concentration that is similar to that used in the most recent linearity study. The response factor of the daily calibration standard is used to quantitate the samples. The batch run will be invalidated for impacted analytes if calibration standard criteria are not met and there is not a valid reason for the deviation, i.e., routine maintenance, retune, etc. If there is enough canister pressure, samples must be re-analyzed after calibration standard criteria are confirmed to be performing appropriately.

17.3. Control Standard

17.3.1. The method control standard is a canister filled with an alternate source gas mixture to verify the operation of the system and as an independent verification of the instrument calibration. This control contains all target compounds, and it is used to maintain QC charts.

Table 1: Daily Quality Control

QC Type	Frequency	Criteria	Suggested Corrective Action
PFTBA Tune	Each time samples are scheduled; must be ran before the calibration standard.	Autotune done by instrument marks as passed and/or meets manufacturer's criteria.	• Check Air/Water and background. • Check level of tune standard. • Adjust parameters to improve sensitivity. • Run a full tune followed by an Autotune. • Clean source. • Contact manufacturer if tuning continues to fail.
CCV/Opening Standard	Analyzed once after the daily tune.	Integration results must be within ± 20% and ± 0.300 minutes of the previous calibration standard response.	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another CCV or prepare new CCV and re-analyze. • If the CCV fails for compound(s) and reanalysis is not possible, may invalidate with NLB management approval. • Re-calibrate if criteria continue to not be met.
Control Standard	Analyzed once after the daily CCV.	Must fall within established control criteria (See Table 2).	• Re-analyze prior to sample analysis once if 24-hour clock has not lapsed, report the second analysis if it is within criteria, and document the reanalysis on the run log and review checklist. • Analyze another control standard or prepare new control standard and re-analyze. • If the control standard fails for select compound(s) and the sample cannot be reanalyzed, those compounds are invalidated with NLB management approval. Document exceedances accordingly. • Re-establish Control Limits.
Method Blank	One (1) per analysis batch after the control standard.	<RL.	• If the method blank result is higher than the RL, the following apply: • If sample results are at least 10x higher than the blank result, it is documented on the daily QC package, but no additional corrective action is required. • If sample results are less than 10x higher than the blank result, the analysis results for those samples are invalid. • The cause of contamination is investigated; the entire batch is re-analyzed if required and if sample is available.

Table 1: Daily Quality Control

QC Type	Frequency	Criteria	Suggested Corrective Action
Check/Closing Standard	Analyzed after 10 or fewer samples and at end of analytical batch.	Integration results must be within ± 20% and ± 0.300 minutes of the CCV response. A CCV and/or a control standard can be used; must be analyzed within 24 hours of first standard.	• 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.
System Blank	Analyzed before CCV/opening standard, before check/closing standard, and after samples with high concentrations due to suspected carryover.	<RL.	• If initial system blank is above RL, additional system blanks can be analyzed to clear the analytical system of possible contamination. See sections 5.1 and 5.2 for interferences and limitations. • If sample results following a system blank with values greater than the RL are at least 10x higher than the blank result, it is documented on the daily QC package, but no additional corrective action is required. • If sample results are less than 10x higher than the blank result, the analysis is repeated if possible or the results for impacted analytes in those samples are invalidated. • The cause of contamination is investigated; the entire batch is re-analyzed if required and if sample is available.

Table 2: Sample Quality Control

QC Type	Frequency	Criteria	Suggested Corrective Action
Sample Pressure	All samples.	≥ 5 psig to ≤16 psig.	• If <5 psig, sample is invalid unless it is a grab (non-flow controlled) sample. • If >16 psig, valid with management approval and document.
Sample Hold Time	All samples.	Analyze within 30 days of collection.	• If sample(s) are analyzed outside hold time, document, and report results.
Duplicate	1 per 10 or fewer samples in analytical batch.	RPD ± 25%.	• If RPD exceeds ± 25%, evaluate. • If primary and duplicate samples have results <5x RL, no need to notify management. Report results. • If both sample results are >5x the RL and the RPD> +/- 25%, re-analyze duplicate and all associated samples in the batch. If still outside criteria, investigate and correct issues, re-analyze. Invalidate all samples in batch if duplicate fails again.
Collocated Samples	10% of field samples or per field protocol.	RPD ± 25%.	• If RPD exceeds ± 25%, evaluate. • If primary and collocated samples have results <5x RL, no need to notify management. Report results. • If both primary and collocated results are >5x RL, notify NLB management, report results and document.
Carryover Check	After analysis of high concentration sample exceeding upper linear range.	No target analytes detected above RL.	• Analyze one or more blanks to clean system. • Re-analyze subsequent sample(s) to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. • Re-analyze high-level sample at a dilution to get target analyte within the linear calibration range. • Report first analysis for all compounds within the calibration range and report the dilution analysis for the compounds that exceeded the calibration range in the initial analysis.
Field Spike	Per client request or field protocol.	70-130% of expected value.	• Re-analyze to confirm results. • Investigate if still outside criteria. • Report results if no analytical issues and control standard meets criteria. • Results outside criteria are documented.

Table 2: Sample Quality Control

QC Type	Frequency	Criteria	Suggested Corrective Action
Control Limits	To be reviewed quarterly for trends and to be re-established as needed or with a new standard.	• Initial warning and control limits shall be set at ±8 and ±10 Percentage Difference respectively from the target value. • Once a minimum of 20 control standard results are obtained, the control limits are set as follows: • ±2 and ±3 std dev of the Mean Value. • Control limits should not exceed ±10% Relative Standard Deviation (RSD) from the calculated mean value. RSD is assigned to ± 5% if the calculated RSD is less than 5%. If the calculated RSD is between 5% and 10%, the actual value is used. If calculated RSD is greater than 10%, an assigned value of ±10% is used. • If the calculated control limits exceed ±10% RSD from the calculated mean value, an assigned %RSD is back calculated based on the assigned %RSD and used for establishing the control limits.	• If three consecutive control standards fell between the warning and control limits, investigation is required. • Evaluate potential cause and investigate, notify management, and come up with corrective action. Document what was done to rectify issue by preparing new standards and/or re-establishing new control limits.

Table 3: Annual Quality Control

QC Type	Frequency	Criteria	Suggested Corrective Action
Calibration Curve	To be established annually at a minimum, when major maintenance or major changes are done or when calibration standard no longer meets criteria.	• Minimum of five upscale calibration points. • Each point ran once. • Linear curve is forced through zero. • Use linear regression with correlation coefficient, R ≥ 0.98 (R^2 > 0.96).	• If the calibration curve fails, re-analyze. Prepare new calibration standards if criteria still not met. • If linear calibration continues to fail, stop, and begin corrective actions to determine the cause of repeated failures, (specifics include instrument maintenance, mixer/diluter issues, and canister issues).
MDL Verification	To be established annually when major maintenance or major changes are done.	• The MDL must be below RL. • Minimum of seven replicates are required. • The seven replicates may be achieved with one canister. • Must meet window criteria of MDL < Spike Concentration < 10x MDL.	• If the MDL is not below RL, the MDL Verification fails and must be evaluated and possibly re-analyzed. • If the MDL is below the RL and does not meet the window criteria, the MDL must be attempted again at a lower spike concentration unless it was performed at the lowest feasible concentration. • If the re-analyzed MDL is below the RL, and still does not meet the window criteria, the MDL may be accepted with management approval. Document what was attempted.

18. CALCULATIONS

18.1. Relative Percent Difference (%RPD) between two results is calculated as follows:

$$\%\text{RPD} = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}\ x\ 100$$

X_1 = First measurement value
X_2 = Second measurement value

18.2. Relative Standard Deviation (RSD) for Control Limits is calculated as follows:

$$\text{RSD} = \frac{S}{\overline{X}}\ x\ 100$$

S = Standard Deviation
$\overline{x}$ = Sample Mean

18.3. Sample Pressurization Dilution Factor (DF) is calculated as follows:

$$\text{DF} = \frac{(psig\ after\ dilution + psia\ lab\ absolute)}{(psia\ lab\ absolute + (vacuum\ inHg\ before\ dilution\ x\ 0.491))}$$

If canister is received at ambient pressure or under vacuum, a conversion factor is multiplied by the vacuum in inHg.

Factor for converting inHg to psig = 0.491

Pounds per square inch absolute (psia) = 14.7

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

$$\%\ \text{Difference} = \frac{Area_{New\ Standard} - Area_{Old\ Standard}}{Area_{New\ Standard}}\ x\ 100\%$$

18.5. Field spike recoveries are calculated as follows:

$$\left(\frac{Field\ spike\ sample\ concentration - Collocated\ sample\ concentration}{Spiked\ Amount}\right) x\ 100\%$$

19. DATA MANAGEMENT AND REPORTING

19.1. 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, archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are always to be kept with the instrumentation.

19.2. After data acquisition, the analytical software processes raw data files to produce result files. The result files contain quantitation information such as peak areas and retention times, along with concentration and instrumentation information.

19.3. Identification of Compounds

19.3.1. 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. Any re-integrations (manual changes to the baseline) amended by the chemist are documented in the instrument processing software

19.3.2. Retention times are visually evaluated to confirm that the peaks are not shifting more than ± 0.300 minutes. If shifting occurs, maintenance may need to be performed and samples re-analyzed.

19.4. Data Transfer to LIMS

19.4.1. Data from the analytical instrument are transferred into LIMS via a data transfer software (i.e., LIMSLink). Data transfer software is also programmed to check results against QC criteria in LIMS before data transfer. Post data transfer, the analyst will review the raw data and QC data transfer and apply corrective action(s) as needed.

19.5. Reporting Results

19.5.1. All data will be reviewed by the analyst, peer reviewed, and management as per the NLB QCM before being released to the client or for entry into the U.S. Environmental Protection Agency's Air Quality System database.

19.5.2. Analyte concentrations will not be reported below the RL unless otherwise requested by the client and approved by lab management.

20. MAINTENANCE AND REPAIRS

Preventative 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 an experienced staff. Any preventive maintenance and/or repairs completed are documented in a logbook stored near the instrument or recorded in the instrument log files.

21. REVISION HISTORY

	Date	Updated Revision	Original Procedure
1	**Description: New SOP for the analysis of VOCs and Oxygenates**		
	May 14, 2021	MLD072 SOP for the analysis of VOC and Oxygenated compounds in ambient air using Gas Chromatography/Mass Spectrometry	New Method

22. REFERENCES

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

22.1.1. NLB Laboratory Quality Control Manual, current version.

22.1.2. MLD020 Standard Operation Procedure for Cleaning Stainless Steel Air Canisters.

22.1.3. MLD058 Standard Operation Procedure for Determination of Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry with Addendum, current version.

22.1.4. MLD066 Standard Operation Procedure for Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry with Addendum, current version.

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

22.2. NLB Chemical Hygiene Plan, current version.

22.3. Saturn 2000 GC/MS, Hardware Operation Manual, Agilent, 2007. http://www.ecs.umass.edu/eve/facilities/equipment/Varian2200/914978.pdf

22.4. Saturn 2000 GC/MS, MS Workstation, Operation Manual, Agilent, May 2010. https://www.agilent.com/cs/library/usermanuals/public/914979.pdf

22.5. Trace 1300 and Trace 1310, Gas Chromatographs, Hardware Manual, Thermo Fisher Scientific, January 2016. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-31715002-GC-TRACE-1300-1310-Hardware-Man31715002-EN.pdf

22.6. Trace 1300 and Trace 1310, Gas Chromatographs, User Guide, Thermo Fisher Scientific, January 2016. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-31715003-GC-TRACE-1300-1310-User-Man31715003-EN.pdf

23. APPENDICES

Appendix 1 (OLS-MLD072-A1): Typical Thermal Desorption Methods for MLD072.

Appendix 2 (OLS-MLD072-A2): Typical GC/MS Methods for MLD072.

Appendix 3 (OLS-MLD072-A3): Target Compounds Validated by MLD072.

Appendix 4 (OLS-MLD072-A4): Example Calibration Levels for VOCs and Oxygenates.

Appendix 5 (OLS-MLD072-A5): Example Certificate of Analyses.

Appendix 6 (OLS-MLD072-A6): Annual SOP Review Log.

Appendix 1

OLS-MLD072-A1

Typical Thermal Desorption Methods for MLD072

Note – These operating conditions are specific to CARB's use of Markes units with a Thermo or Agilent GC/MS. This section also covers the sample delivery system for the Saturn GCMS. Method parameters may change if needed by an experienced analyst and by management approval.

Markes units with a Thermo or Agilent GC/MS

Standby – Split On; 30 mL/min
Leak Test – On
Flow Path – 160°C
GC Cycle Time – 53 minutes
Minimum Carrier Pressure – 1 psi

Pre-Sampling Tab:
Sample Purge Time – 2.0 minutes at 50 mL/min
Kori Trap Low – -30°C
Kori Trap High – 300°C

Sampling Tab:
Sample by Volume – Yes
Sample Quantity – 300 mL/min
Post Sampling Purge Time – 5 minutes at 50 mL/min

Post-Sampling Tab:
Trap Purge – 3 minutes at 50 mL/min
Trap Low – 30°C
Trap High – 240°C
Trap Heating Rate (°C/s) – MAX
Trap Hold – 1 minute; split on; 20 mL/min

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

Kori-xr Trap Purge Flow – approx. 100 mL/min

Load Volume: 300 mL

Sample Delivery System Temperature Zones for a Varian Saturn GCMS

Zone 1: Front Injector 1079 (carbon trap)

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	145.0	9.00	9.00
200.0	275.0	52.35	62.00

Zone 2: Middle Injector 1079 (cryofocuser)

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	200.0	2.00	2.00
200.0	-30.0	9.85	13.00
200.0	250.0	47.60	62.00

Zone 3: Middle Valve – (sample lines)

Rate (mL/min/min)	Flow (mL/min)	Hold Time (minutes)	Run Time (minutes)
0.00	1.60	52.00	52.00
2.00	2.00	9.80	62.00

Zone 4: Front FID- Not used

Zone 5: Middle FID - valve oven with SSV 80C

Zone 6: Front Valve - 2 valve oven 150C

Helium Output Pressure – approx. 80 psi
Nitrogen Output Pressure – approx. 60 psi

Liquid Nitrogen Dewar Pressure Range – approx. 35-50psi

Load Volume: 150 mL

Appendix 2

OLS-MLD072-A2

Typical GC/MS Methods for MLD072

Note – these operating conditions are specific to CARB's use of an Agilent, Thermo, or Saturn GC/MS. Method parameters may change if needed by an experienced analyst and by management approval.

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 – Off
Front Inlet Flow – 1.200 mL/min
GC Standby Temp – 100°C

Thermo Column Oven Parameters:

Retention Time (minutes)	Rate (°C/min)	Target Value (°C)	Hold Time (minutes)
5.00	0.00	35.0	5.00
33.0	5.00	170.0	1.00
39.25	40.00	220.0	5.0

Thermo MS Parameters:

Ion Source (Thermo MS) – 330°C
MS Transfer Line – 230°C
Ionization Mode – EI

Segment	Time (minutes)	Range (amu)	Dwell/Scan Time (seconds)	Total Scan (seconds)	Filament On	Detector Gain
1	4.25	47-200	0.15	0.154	YES	$3.00x10^5$
2	5.00	50, 53, 54, 62, 64	0.15, 0.15, 0.15, 0.15, 0.15	0.9244	YES	$3.00x10^5$
-----	-----	47-200	0.15	0.154	YES	$3.00x10^5$
3	6.00	47-200	0.15	0.154	YES	$3.00x10^5$
4	8.00	42, 43, 44, 45, 46	0.15, 0.15, 0.15, 0.15, 0.15	0.9244	YES	$3.00x10^5$
-----	-----	35-200	0.15	0.154	YES	$3.00x10^5$
5	8.85	35-200	0.15	0.154	YES	$3.00x10^5$
6	27.00	35-200	0.15	0.154	NO	$3.00x10^5$

Agilent GC Parameters:
Front Inlet – 40°C
Front Inlet Pressure Mode – On
Front Inlet Pressure Control – 15 psi
Total Flow – 102.89 mL/min
Purge Flow to Split Vent – 100 mL/min at 999.99 minutes
Front Inlet Split Mode – Splitless
Initial Flow at Beginning of Run – 2.393 mL/min at 35°C
GC Standby Temp – 100°C

Agilent Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	35.0	5.00	5.00
5.00	135.0	1.00	26.00
40.00	220.0	4.875	33.00

Agilent MS Parameters:
Ion Trap (Agilent MS) – 150°C
MS Transfer Line – 170°C
Ionization Mode – Internal EI
Mass Data Type – Centroid
Target TIC – 30000 counts
Max Ion Time – 35000 µSeconds
Emission Current – 40 µAmps
Scan Type – Full
Number of Segments – 4
Scan Speed – Normal
Offset – 100

Segment	Time (minutes)	Range (amu)	Low Mass (m/z)	High Mass (m/z)	Storage Level (m/z)	Ion Time Factor (%)	Filament On
1	0-3.00	none	10	99	35	35	OFF
2	3.00-5.26	49-190	100	249	35	35	ON
3	5.26-26.00	35-190	250	399	35	35	ON
4	26.00-33.00	none	400	1000	35	35	OFF

Saturn 3800 GC Parameters:
Front Inlet – 50°C
Front Inlet Pressure Mode – On
Front Inlet Pressure – 12 psi
Linear Velocity – 40.5 cm/sec
Initial Flow at Beginning of Run – 1.6 mL/min at 100°C
GC Standby Temp – 100°C
Coolant Timeout – 60min
Coolant Used – Liquid Nitrogen

Saturn 3800 Column Oven Parameters:

Rate (°C/min)	Target Value (°C)	Hold Time (minutes)	Run Time (minutes)
0.00	100.0	8.20	8.20
100.0	-20.0	3.60	13.00
4.00	140.0	0.00	53.00
100.0	200.0	8.40	62.00

Saturn 2000 MS Parameters:
Ion Trap (Saturn MS) – 150°C
MS Transfer Line – 170°C
Manifold – 50°C
Ionization Mode – EI AGC
Mass Data Type – Centroid
Target TIC – 20000 counts
Max Ion Time – 25000 µSeconds
Background mass – 33m/z
RF Dump Value – 650m/z
Emission Current – 30 µAmps
Scan Type – Full
Number of Segments – 2
Scan Speed – Normal
Offset – none

Segment	Start Time (minutes)	End Time (minutes)	Range (amu)	Low Mass (m/z)	High Mass (m/z)	Storage Level (m/z)	Ion Time Factor (%)	Filament On
1	0.00	4.00	10-99	40	650	32	100	NO
2	4.00	49.00	100-249	33	200	32	100	YES

Appendix 3

OLS-MLD072-A3

Target Compounds Validated by MLD072

Compounds	RL (PPB)	CAS Number
Dichlorodifluoromethane (Freon 12)	0.020	75-71-8
Vinyl Chloride	0.020	75-01-4
1,3-Butadiene	0.040	106-99-0
Bromomethane	0.030	74-83-9
Trichlorofluoromethane (Freon 11)	0.010	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	0.020	76-13-1
Dichloromethane	0.100	75-09-2
Chloroform	0.020	67-66-3
Methyl Chloroform	0.010	71-55-6
Carbon Tetrachloride	0.020	56-23-5
Benzene	0.050	71-43-2
Trichloroethylene	0.020	79-01-6
cis-1,3-Dichloropropene	0.100	10061-01-5
Toluene	0.200	108-88-3
trans-1,3-Dichloropropene	0.100	10061-02-6
Tetrachloroethylene	0.010	127-18-4
Ethylbenzene	0.200	100-41-4
m/p-Xylene	0.200	108-38-3 106-42-3
o-Xylene	0.100	95-47-6
Styrene	0.100	100-42-5
Acrolein	0.300	107-02-8
Acetone	1.000	67-64-1
Acetonitrile	0.300	75-05-8
Acrylonitrile	0.300	107-13-1

Appendix 4

OLS-MLD072-A4

Example Calibration Levels for VOCs

Mid-Point 2.000 PPB

LEVELS OF CONCENTRATION (PPB)								
DF	1/10000	1/3220	1/970	1/324	1/100	1/50	1/30	1/20
PPB	0.010	0.031	0.103	0.309	1.000	2.000	3.330	5.000

Example Calibration Levels for Oxygenates

Mid-Point at DF 0.02

DF	**Acrolein (PPB)**	**Acetone (PPB)**	**Acetonitrile (PPB)**	**Acrylonitrile (PPB)**
0.0004	0.100	0.370	0.0925	0.0929
0.0008	0.200	0.740	0.185	0.186
0.0025	0.600	2.220	0.555	0.558
0.0067	1.600	5.920	1.480	1.487
0.013	3.200	11.840	2.960	2.973
0.02	4.800	17.760	4.440	4.460
0.033	8.000	29.660	7.400	7.433
0.05	12.000	44.400	11.100	11.150

Appendix 6

OLS-MLD072-A6

Annual SOP Review Log

By signing this form, the analyst acknowledges that her or she understands the method SOP and follows the procedures when performing the associated analyses. Management initials each line to ensure changes and comments are communicated.

Review Date	Reviewed By	First Time Review? Yes/No	Changes Needed	Comments	Management Initials