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

MLD072
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Northern Laboratory Branch
Monitoring and Laboratory Division

| Approval Signatures | Approval Date |
|---|---|
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## 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.<br>• Check level of tune standard.<br>• Adjust parameters to improve sensitivity.<br>• Run a full tune followed by an Autotune.<br>• Clean source.<br>• 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.<br>• Analyze another CCV or prepare new CCV and re-analyze.<br>• If the CCV fails for compound(s) and reanalysis is not possible, may invalidate with NLB management approval.<br>• 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.<br>• Analyze another control standard or prepare new control standard and re-analyze.<br>• 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.<br>• 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:<br>• 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.<br>• If sample results are less than 10x higher than the blank result, the analysis results for those samples are invalid.<br>• 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.<br>• 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.<br>• 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.<br>• 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.<br>• 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.<br>• 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.<br>• 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.<br>• If primary and duplicate samples have results <5x RL, no need to notify management. Report results.<br>• 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.<br>• If primary and collocated samples have results <5x RL, no need to notify management. Report results.<br>• 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.<br>• Re-analyze subsequent sample(s) to confirm results are not biased high due to contamination from analysis of preceding high concentration sample.<br>• Re-analyze high-level sample at a dilution to get target analyte within the linear calibration range.<br>• 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.<br>• Investigate if still outside criteria.<br>• Report results if no analytical issues and control standard meets criteria.<br>• 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.<br>• Once a minimum of 20 control standard results are obtained, the control limits are set as follows:<br>• ±2 and ±3 std dev of the Mean Value.<br>• 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.<br>• 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.<br>• 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.<br>• Each point ran once.<br>• Linear curve is forced through zero.<br>• Use linear regression with correlation coefficient, $R \geq 0.98$ ($R^2 > 0.96$). | • If the calibration curve fails, re-analyze. Prepare new calibration standards if criteria still not met.<br>• 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.<br>• Minimum of seven replicates are required.<br>• The seven replicates may be achieved with one canister.<br>• 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.<br>• 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.<br>• 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 (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

## 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 – 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 (ºC/min) | Target Value (ºC) | 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 | $3.00x10^5$ |
| 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 – 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 |

## 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<br>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 |
|---|---|---|---|---|---|
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