Standard Operating Procedure for the Determination of Compounds Found in Consumer Products Using Gas Chromatography

SAS07
Revision 2.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph. D., Chief Quality Management Branch	10/31/2023
Michael Werst, Chief Northern Laboratory Branch	11/16/2023

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

1 SCOPE 1
2 SUMMARY OF METHOD 1
3 ACRONYMS 1
4 DEFINITIONS 3
5 INTERFERENCES 3
6 PERSONNEL QUALIFICATIONS AND TRAINING 4
7 SAFTEY REQUIREMENTS 4
8 HAZARDOUS WASTE 4
9 EQUIPMENT AND SUPPLIES 5
10 CHEMICALS AND GASES 6
11 STANDARD PREPARATION 6
12 ANALYTICAL PROCEDURE 8
13 QUALITY CONTROL 11
14 CALCULATIONS 13
15 SAMPLE AND DATA MANAGEMENT 13
16 TROUBLESHOOTING, SERVICE REPAIRS, AND MAINTENANCE 14
17 REVISION HISTORY 15
18 REFERENCES 16
19 APPENDICIES 17

List of Tables

Table 1. Summary of Acronyms 1
Table 2. Definitions of Terms 3
Table 3. Calibration sample preparation from 80 mg/mL stock.. 7
Table 4. Calibration sample preparation from 100 mg/mL stock.. 7
Table 5. Daily Quality Controls 12
Table 6. Annual Quality Controls 13
Table 7. Revision History Summary 15

List of Equations

14.1. Equation 1. Weight fraction of a compound. 13
14.2. Equation 2. Average of replicate pairs. 13
14.3. Equation 3. Relative Percent Difference (%RPD) between two results. 13

Standard Operating Procedure for the Determination of Compounds Found in Consumer Products Using Gas Chromatography

1 SCOPE

This standard operating procedure (SOP) is used for the measurement of target compounds in a non-aerosol or the non-propellant portion of an aerosol consumer product, following Method 310 (18.2) as required by the Consumer Products Regulations (18.1). Development of this SOP was aided by procedures specified in United States Environmental Protection Agency (U.S. EPA) Method 18, National Institute of Occupational Safety and Health (NIOSH) Method 1400, NIOSH Method 1401, NIOSH Method 1402, NIOSH Method 1403, and U.S. EPA Method 8240B. All procedures and regulations referenced herein may be found in the *REFERENCES* section. The analysis of certain target compounds is subject to the supply of the chemical standard. The option to procure may be limited or not at all. See *Appendix 3* for a list of target compounds analyzed in this method. This standard operating procedure (SOP) was developed by staff in the Special Analysis Section (SAS) of the Northern Laboratory Branch (NLB).

2 SUMMARY OF METHOD

Sample dilutions, as prepared by SAS14 (18.5), are analyzed by a gas chromatograph (GC) equipped with a flame ionization detector (FID). Results are generated in milligrams per milliliter (mg/mL) and the data is reported as a weight fraction of a target compound in a non-aerosol or the non-propellant portion of an aerosol consumer product.

3 ACRONYMS

Table 1. Summary of Acronyms

ACS	American Chemical Society
ALS	Automatic Liquid Sampler
AMP	aminomethyl propanol
CARB	California Air Resources Board
CHP	Chemical Hygiene Plan
DCM	dichloromethane
DIPROP	dipropylene glycol
DMCPS	decamethylcyclopentasiloxane
DMTS	decamethyltetrasiloxane
EG	ethylene glycol
FID	Flame ionization detector
GC/FID	Gas Chromatograph with Flame Ionization Detector
GC/MS	Gas Chromatograph with Mass Spectrometer
He	Helium

HMCTS	hexamethylcyclotrisiloxane
HMDS	hexamethyldisiloxane
Hz	Hertz (sec^{-1})
i.d.	inner diameter
ID	identification
IPA	isopropyl alcohol
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation
MDL	Method Detection Limit
MEK	methyl ethyl ketone
µm	Micrometers (micron)
mg/mL	Milligram per milliliter (concentration unit)
mL/min	Milliliters per minute (flow)
mm	Millimeters
MLD	Monitoring and Laboratory Division
MPA	1-methoxy-2-propanol
MS	Mass Spectrometer
NCCLS	National Committee for Clinical Laboratory Standards
NIOSH	National Institute of Occupational Safety and Health
NLB	Northern Laboratory Branch
OMCTS	octamethylcyclotetrasiloxane
OMTS	octamethyltrisiloxane
pA	picoamp
psi	pounds per square inch
PDCB	paradichlorobenzene
PERC	perchloroethylene
PG	propylene glycol
PM	Preventative Maintenance
PM acetate	propylene glycol methyl ether acetate
QC	Quality Control
QCM	Quality Control Manual
RL	Reporting Limit
RPD	Relative Percent Difference
SAS	Special Analysis Section
sd	Standard Deviation
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
TCE	trichloroethylene
UHP	Ultra-High Purity
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound(s)

4 DEFINITIONS

Table 2. Definitions of Terms

Term	Definition
ACS Grade	Chemicals meeting standards set by the American Chemical Society.
aliquot	A representative portion of a non-aerosol sample or the non-propellant portion of an aerosol sample.
analytical batch	A set of samples analyzed together as a group for a particular analysis.
Batch Sample	A laboratory prepared sample aliquot of known concentration for QC evaluation under Method 310.
Control/Check standard	A quality control standard prepared from a source different from the calibration standards. This QC standard is also separately identified as a Control standard and a Check standard.
duplicate	A second analysis of a sample submitted for analysis under Method 310.
duplicate aliquot	An additional sample aliquot from the same sample carried through all steps of the sampling and analytical procedures of Method 310 in an identical manner.
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
Replicate	An additional analysis of the same sample aliquot or sample dilution.
sample	The sample submitted for analysis under Method 310.
sample aliquot	The sample aliquot is any aliquot used for analysis, and includes the duplicate aliquot, the Batch Sample, or any archive aliquot undergoing a re-test.
sample batch	A set of samples analyzed together under Method 310.
sample dilution	Dilution made from the sample aliquot (prepared per SAS14).
solvent blank	A blank consisting of reagent(s), used in the sample dilutions, without the target compound(s), analyzed to determine interferences or contamination during analysis.

5 INTERFERENCES

5.1 With the increase in the number of target compounds being identified, overlap of the retention times may start to occur. Target compounds can coelute with the solvent or other interferences. Care must be taken to make certain of the identity of the compounds, if possible, through headspace gas chromatography/mass spectrometry analysis SAS06 (18.3).

5.2 There are some instances where another solvent may be required for a

particular analysis as 1-methoxy-2-propanol (MPA) may interfere with the compound of interest (e.g., trichloroethylene uses the solvent hexane). In these cases, all blanks, Control/Check standards, calibration standards, and samples are to be prepared using this same alternate solvent, in addition to the MPA dilutions.

6 PERSONNEL QUALIFICATIONS AND TRAINING

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

7 SAFTEY REQUIREMENTS

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

7.2 Analysts should acknowledge any sample labeling for safety warnings and take appropriate safety measures.

7.3 Wear appropriate PPE and review all associated Safety Data Sheets (SDS).

7.4 Ensure engineering controls are in place and operational (i.e., adequate ventilation, proper fume hood, snorkel, and balance enclosure face velocity).

7.5 Follow safe handling practices for compressed gas cylinders.

7.6 The GC/FID has a heated oven, inlets, and detectors that can exceed 250°C. Use caution when operating the instrument and be cautious of invisible flames that can result in a fire hazard or burn.

8 HAZARDOUS WASTE

8.1 Discard used autosampler vials in the satellite hazardous waste accumulation area in the "Consumer Product GC Vial Waste" container. Dispose of satellite hazardous waste in accordance with the NLB CHP.

8.2 Dispose of automatic liquid sampler (ALS) rinse waste in the satellite

hazardous waste accumulation area in the “Consumer Product Waste” container. Dispose of satellite hazardous waste in accordance with the NLB CHP.

9 EQUIPMENT AND SUPPLIES

9.1 Gas Chromatograph configured with a Flame Ionization Detector.

9.2 GC mid-polar column: J & W DB-624, 30 m x 0.32 mm i.d. with 1.80 µm film, or equivalent.

9.3 GC PEG column: Restek Rtx-Stabliwax, 30 m, 0.53 mm i.d., 1.00 µm nominal film thickness, or equivalent.

9.4 GC liner: 4 mm, split, straight wool, Ultra Inert or equivalent.

9.5 Volumetric flasks, Class A, various sizes, 1 mL – 250 mL.

9.6 Pipettors, ranging 10 µL – 5000 µL with tips.

9.7 Pasteur pipettes, disposable with bulbs.

9.8 Transfer pipettes, disposable.

9.9 Volumetric pipettes, Class A, various sizes with bulb.

9.10 4 mL, 8 mL, and 20 mL screw top vials with caps.

9.11 2 mL autosampler vials with caps.

9.12 Autosampler vial cap crimper.

9.13 Autosampler vial cap de-crimper.

9.14 Vial inserts.

9.15 Top-Loader balance, capacity of at least 1000 g x 0.001 g (readability).

9.16 Analytical balance, capacity of at least 220 g x 0.01 mg or 0.10 mg (readability).

9.17 Software for data collection (e.g., Excel, LabX, OpenLab ChemStation, OpenLab CDS, Chromeleon CDS, BalanceTalk, WinWedge, or equivalent).

9.18 Vortex mixer, variable speed.

10 CHEMICALS AND GASES

Consult the latest version of the Quality Control Manual (QCM) for the standard analyte requirements.

10.1 Ultra-High Purity (UHP) Helium, grade 5.

10.2 Hydrogen (compressed cylinder or generator).

10.3 UHP Air (compressed cylinder or generator).

10.4 1-methoxy-2-propanol (MPA), 99+%, dry.

10.5 Hexane, ≥ 98 %.

10.6 Target analytes are listed in *Appendix 3*

11 STANDARD PREPARATION

11.1 Standards used to prepare stock solutions may be prepared from ACS grade or better reagents or purchased as certified solutions. The expiration date for all standards prepared shall be three years from the date of preparation, or the expiration date of the reagents or stock solution from which they are prepared, whichever is sooner.

11.2 Preparing an 80mg/mL Calibration Standard Stock (*Appendix 4*).

11.2.1 Prepare an 80 mg/mL calibration stock standard by accurately weighing and transferring 20.0000 g of each reagent into a 250 mL volumetric flask and bring to volume with the solvent used in sample dilutions in SAS14 (18.5). Dilutions in SAS14 are prepared using MPA as the solvent. Mix well. Alternative volumes may be prepared with the same final concentration.

11.2.2 Fill 20 mL screw top vials with the calibration stock and cap.

11.2.3 Label each vial with “[method name] Calibration Stock [concentration level]” (e.g., “DCM Calibration Stock 80 mg/mL”), preparation date, expiration date, and the preparer’s initials.

11.2.4 There are some instances where another solvent may be required for a particular analysis as MPA may interfere with the compound of interest (e.g., trichloroethylene uses the solvent hexane). In these cases, all blanks, Control/Check standards, calibration standards, and samples are to be prepared using this same alternate solvent.

11.3 Preparing Standards for an 80mg/mL Calibration Curve (*Appendix 4*).

11.3.1 Prepare a calibration curve from the calibration stock standard. Pipette stock standard into 10 mL volumetric flasks and bring to volume with solvent as follows or use serial dilution.

Table 3. Calibration sample preparation from 80 mg/mL stock.

Volume of calibration stock	GC Method Calibration Standard Concentration
12.5 µL	0.1 mg/mL
125 µL	1 mg/mL
1250 µL	10 mg/mL
2500 µL	20 mg/mL
5000 µL	40 mg/mL
n/a (stock)	80 mg/mL

11.4 Preparing a 100mg/mL Calibration Standard Stock (*Appendix 5*).

11.4.1 Prepare a 100 mg/mL calibration stock standard by accurately weighing and transferring 10.0000 g of each reagent into a 100 mL volumetric flask and bring to volume with the appropriate solvent. Mix well. Alternative volumes may be prepared with the same final concentration.

11.4.2 Fill 20 mL screw top vials with the calibration stock and cap.

11.4.3 Label each vial with “[method name] Calibration Stock [concentration level]” (e.g., “TCE Calibration Stock 100 mg/mL”), preparation date, expiration date, and the preparer’s initials.

11.5 Preparing Standards for a 100mg/mL Calibration Curve (*Appendix 5*).

11.5.1 Prepare a calibration curve from the calibration stock standard. Pipette stock standard into 10 mL volumetric flasks, and bring to volume with solvent as follows or use serial dilution:

Table 4. Calibration sample preparation from 100 mg/mL stock.

Volume of calibration stock	GC Method Calibration Standard Concentration
10 µL	0.1 mg/mL
100 µL	1 mg/mL
1000 µL	10 mg/mL
2000 µL	20 mg/mL
5000 µL	50 mg/mL
n/a (stock)	100 mg/mL

11.6 Preparing Control/Check Standard (*Appendix 4* and *Appendix 5*) and Sample Dilutions.

11.6.1 Prepare the Control/Check standard dilution using SAS14 from a stock solution of 250% target compound. Stock solutions may be purchased as certified solutions (purchased chemicals that come with a Certificate of Analysis) or prepared as follows:

- Prepare the Control/Check standard stock solution (250 mg/mL) by weighing 25.0000 g of the specified target compound(s) into 100 mL volumetric flask and bring to volume with solvent. Mix by inversion. An alternative volume may be prepared with the same final concentration.
- Fill 4 mL screw top vials with no less than 1.5 mL and no more than 3.0 mL each of the Control/Check standard stock and cap.
- Label each vial with “[method name] Control/Check,” concentration level, preparation date, expiration date, and the preparer's initials.
- Store the Control/Check standard aliquots under refrigeration. Stored aliquots may be used. It is not necessary to prepare a new stock for each analysis.

11.6.2 Prepare sample dilutions using SAS14.

12 ANALYTICAL PROCEDURE

12.1 Analysis Preparation

12.1.1 Enter the analytical batch into LIMS following procedures outlined in the LIMS Manual. LIMS will randomly assign a replicate for the analytical batch.

12.1.2 Prepare the analytical batch for analysis either using 2 mL autosampler vials prepared in SAS14 or by transferring sample dilutions, Control/Check standard dilutions, and solvent blank(s) prepared in SAS14 to new 2 mL autosampler vials and cap.

12.1.3 Transfer calibration standards prepared in Section 10 to appropriately labeled 2 mL autosampler vials and cap.

12.2 Instrument Preparation

12.2.1 Ensure there is sufficient air and He for the analytical sequence.

12.2.2 Change the tank when the pressure regulator indicates 500 psi or less.

12.2.3 Ensure the output pressure of air (~80 psi) and carrier/makeup gas He (~80-100 psi) leaving the tanks is sufficient to maintain the flows required for the method.

12.2.4 Set pressures may vary depending on the number of instruments drawing from the gas source and the instrument manufacturer's recommendations.

12.2.5 Verify the hydrogen gas supply is adequate.

- Add water to the hydrogen generator reservoir if water source is not plumbed directly prior to analysis.

- Ensure the output pressure of hydrogen (min. ~60 psi) leaving the generator is sufficient. Pressures may vary depending on the number of instruments drawing from the gas source, the instrument manufacturer's recommendations, or the application (e.g., use of hydrogen carrier gas).

12.2.6 Prepare the ALS: Fill solvent rinse vials with appropriate solvent required for analysis and ensure that the waste vials are empty.

12.3 Instrument Method

Analytical method data acquisition parameters are shown in the Appendix section as *SAS07-A1* and *SAS07-A2*. The list of target compounds evaluated under this SOP are listed as *SAS07-A3*.

12.4 Create a Sequence

12.4.1 The following sequence should be submitted with a maximum of ten samples (including duplicates, replicates, and additional injections) and must be bracketed with a solvent blank and Control standard at the start, and a solvent blank and Check standard at the end, for the sequence to be considered valid and reportable. Below is the required order of analysis for a valid sequence:

- Solvent Blank
- Calibration Curve
- Solvent Blank
- Control Standard
- Sample Dilutions (up to 10)
- Solvent Blank
- Check Standard
- Standby Method

12.4.2 Repeat Sample dilutions, solvent blank, and Check standard, as necessary.

12.4.3 Verify the following parameters in the sequence:

- Sample location
- Sample names
- Method name
- Injector location
- Injection source
- Number of injections (2 for the sample assigned as replicate, 1 for all others)
- Sample type (i.e., calibration for the calibration standards, and sample for samples)
- For the calibration standards:
    - Calibration levels
    - Response factors will be replaced
    - Retention times will be averaged

12.4.4 Verify the instrument is directed to go into standby mode at the end of the sequence.

12.4.5 Verify analyst initials are associated with the analytical sequence.

12.4.6 Save and print the sequence.

12.5 Sample Analysis

12.5.1 Place the vials in the ALS, matching the sample location in the sequence. It is not necessary to prepare a separate vial for each solvent blank and Control/Check standard.

12.5.2 Run the sequence.

12.5.3 Print and review the chromatograms and the calibration curve

in hardcopy or digital format (e.g., pdf or equivalent).

12.5.4 Verify the data has met the QC criteria in Section 13 *Table 5*.

12.5.5 Any anomalies occurring during the analysis that affect the data shall be documented on the raw data and in the instrument logbook. All affected samples shall be reanalyzed. If anomalies continue, notify management immediately, and proceed under their direction.

12.5.6 Any instrument issues, repairs, troubleshooting, and/or maintenance shall be documented in the instrument logbook.

12.5.7 Upload to LIMS (refer to LIMS Application: GC Analysis). LIMS will average results of replicate pairs for reporting purposes (*Equation 2*).

12.5.8 Upon completion of analyses, remove 2 mL autosampler vials from the ALS, and ensure the instrument is in standby mode.

13 QUALITY CONTROL

13.1 Several types of QC samples are evaluated daily, annually, or as needed. These are described in Table 5 and 6 below.

13.2 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.

13.3 MDL/LOQ (limit of quantitation) verifications should be performed at least annually. As part of the verification, an LOQ is calculated and compared to the RL. Prepare MDL sample in the appropriate solvent at the concentration of the lowest calibration point. For methods with large numbers of analytes, one standard may be chosen to represent a class or group of similar analytes. Analyze a minimum of seven replicates. The seven replicates may be achieved with one vial. Calculate the MDL as describe in the QCM.

Table 5. Daily Quality Controls

QC Type	Frequency	Criteria	Suggested Corrective Action
Solvent Blank	At minimum before the Control and before each Check.	< RL	• If the blank result is < the RL, no action is taken. • If the blank result is ≥ the RL, and the affected samples are at least ten (10) times higher than the blank value, then no action is taken. • If the blank is ≥ the RL and the sample result is < than ten (10) times higher than the blank value, then the result for the affected samples shall be invalid and the cause investigated. • The affected samples may be re-prepared and analyzed.
Calibration Curve	Each analytical batch.	Correlation coefficient of greater than 0.98.	• If criterion is not met, reanalyze the calibration curve or make up a new calibration curve. • Reanalyze the analytical batch after a successful calibration.
Control/ Check Standard	The Control is analyzed after the calibration and Check standard after every ten or fewer samples and at the end of the analytical sequence.	Warning and control limits are set at ±8 and ±10 percent difference respectively from the target value.	• If an analysis is out of the control limits, the affected sample result(s) are invalid. • Evaluate potential cause and investigate (see ***troubleshooting***), notify management, and come up with corrective action. Document what was done to rectify issue. • Three consecutive Control standards falling between the warning and control limits require investigation and corrective action as described in the QCM.
Replicate	One of ten or fewer samples in the analytical batch.	For replicate results ≥ 5 x RL: RPD ≤ 25	• Reanalyzed if enough sample is available. • Invalidated if reanalysis is not possible.
Duplicate	One of ten or fewer samples in the sample batch	No QC criteria for this SOP. Evaluate duplicate results after calculating total VOC per SAS13.	• Not applicable. Refer to SAS13 for overall % VOC criteria.

Table 6. Annual Quality Controls

QC Type	Frequency	Criteria	Suggested Corrective Action
MDL Verification	To be established annually, or when major maintenance or major changes are done.	• The MDL must be below RL.	• If the MDL is not below RL, the MDL Verification fails and must be evaluated and possibly re-analyzed.
Balances	Calibrated annually. Daily verification done prior to use.	• Annual calibration to be performed by an outside source. • ±2sd respectively from the target value for daily verification.	• Manually recalibrate the balance per manufacturers specifications. • Notify management and contact service provider for recalibration and/or repair.

14 CALCULATIONS

Calculations are automatically calculated in LIMS.

14.1. Equation 1. Weight fraction of a compound.

$$\text{Weight Fraction Compound} = \frac{\text{Compound (mg/mL)}}{\text{sample dilution weight (g)/10 mL}} \times \frac{1\text{ g}}{1000\text{ mg}}$$

14.2. Equation 2. Average of replicate pairs.

$$\text{Average} = \frac{X+Y}{2}$$

14.3. Equation 3. Relative Percent Difference (%RPD) between two results.

$$\%\text{RPD} = \frac{(Y-X)}{((Y+X)/2)} \times 100$$

X = the sample result
Y = the duplicate result

15 SAMPLE AND DATA MANAGEMENT

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

15.2 Sample and data management follow procedures outlined in the QCM. The LIMS Manual describes data management procedures as they pertain to LIMS for this SOP. Additional SOPs that cover sample and data management as they pertain to sample preparation and data reporting under Method 310 include SAS13 (18.4) and SAS14 (18.5).

15.3 Information that has been designated as confidential, proprietary, or trade secrets must be maintained in a locked file cabinet in a secure area. Access to this file cabinet is subject to management approval.

16 TROUBLESHOOTING, SERVICE REPAIRS, AND MAINTENANCE

Basic troubleshooting can consist of changing the gas absorbent traps, ALS syringe, ALS needle guide, septum nut, inlet septum, inlet liner, liner O-ring, gold seal, column nut, column ferrule, column, detector nut, detector ferrule, FID jet, FID ignitor, split vent traps, and lines or other consumables.

16.1 Externally and internally check the system for leaks and measure flow with a flow meter at the split vent or septum purge vent.

16.2 Column cutting and re-installation is permitted.

16.3 Baking out or conditioning inlet, oven and detectors is permitted.

16.4 Consult the instrument manufacturer’s online database of instructional videos for assistance performing tasks.

16.5 Utilize the Agilent 8890 GC built-in intelligence with step-by-step instruction for common maintenance procedures.

16.6 Reference the troubleshooting manual published by the manufacturer that is associated with the specific model of gas chromatograph (i.e., Agilent 6850, 7890A, 7890B, 8890, Intuvo 9000, etc.) or ALS (i.e., Agilent 6973A, 7650A, 7683, etc.) for other detailed troubleshooting efforts.

16.7 Contact the instrument manufacturer’s customer support call center for assistance. (i.e., Agilent Technologies, 1-800-227-9770).

16.8 Service repairs and preventative maintenance (PM) are performed by contractors.

17 REVISION HISTORY

Table 7. Revision History Summary

SOP/Addendum Identification	Approval Date	Description of Change
MLD - 306	May 16, 1996	Original Procedure
SOP MLD ES07 Revision 2	March 10, 1998	Adjusted document font to Times New Roman 12. Inserted appendix B formerly a stand-alone document.
SOP MLD ES07 Revision 3	February 3, 1999	Addition of exempt compounds in the calibration files. This also includes modifications to Appendix A to include additional analyses for some less common exempts and aromatic hydrocarbons.
Unknown	February 4, 2003	Inserted Appendix C the Siloxane procedure and Appendix D the MEK procedure. Renamed the DCM procedure Appendix B and renamed the Acetone procedure Appendix A. Adjusted document font to Times New Roman 12. Renumbered to new section number.
Unknown	April 3, 2003	Modified all Appendices to reflect calibration curve changes, and calibration standard preparation. Modified calibration range for MEK and Siloxane, now to include a high point of 80 and 50 percent respectively. Modified Acetone/Alcohol standard prep exception including ethanol and isopropanol. Current neat ethanol is denatured with methanol.
MLD SOP SAS07 Revision 1.5	January 7, 2005	Inserted Appendix E, the Glycol procedure. Retitled to reflect the scope covered by SOP. Changed document font to Arial 12. Corrected revision enumeration.
SAS07 Revision 1.6	January 18, 2005	Added Glycerol and Butyl Carbitol to the Glycol procedure (Appendix E).
SAS07 Revision 1.7	June 1, 2007	Update for all methods. Revised Glycols which now uses a different column and is itself divided into 2 methods.
SAS07 Revision 1.8	August 20, 2010	Update of methods. Addition of hexylene glycol analysis, as Appendix F.
SAS07 Revision 1.9	August 28, 2012	Update of methods. Addition of dipropylene glycol analysis to Appendix E.
SAS07 Revision 2.0	November 16, 2023	Reviewed for grammar, content, and compliance with the most recent versions of the QCM Manual and MLD076. Added new QC measure replicate with criteria and corrective action. Replaced the “Trip Sample” with “Batch Sample.” Deleted repetitive alphabetical appendices. Updated the References section. Revised to include previously approved methods: TCE and PDCB. Removed 1,1,1-trichloroethane from the DCM method to a single analyte method named 1,1,1-TRICHLOROETHANE. Added lists of tables and equations. Added section for Troubleshooting, Service Repairs and Preventative Maintenance. Improved formatting, readability, and organization.

18 REFERENCES

18.1 The California Consumer Product Regulations, Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Article 1-5, Sections 94500-94575, August 1, 2022, (or most current version).

18.2 Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds (ROC) in Aerosol Coating Products, August 1, 2022, (or most current version).

18.3 SAS06 Standard Operating Procedure for the Tentative Identification of Compounds in Consumer Products by Headspace Gas Chromatography/Mass Spectrometry, Revision 1.5, October 28, 2021, (or most current version).

18.4 SAS13 Standard Operating Procedure for Consumer Product Sample Batch Management and Reporting, Revision 0.0, August 5, 2019, (or most current version).

18.5 SAS14 Standard Operating Procedure for Consumer Product Sample Preparation, Revision 0.0, August 5, 2019, (or most current version).

18.6 CARB NLB Laboratory Quality Control Manual, Revision 5.0, December 7, 2021, (or most current version).

18.7 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 1.0, December 30, 2021, (or most current version).

18.8 CARB, Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street, June 17, 2022 (or most current version).

18.9 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS), December 20, 2022 (or most current version).

18.10 U.S. EPA Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, Title 40 CFR Part 60, Appendix A, (July 1, 1996).

18.11 NIOSH: Methods 1400, Alcohols I, NIOSH Manual of Analytical Methods, Fourth Edition, (August 15, 1994).

18.12 NIOSH: Method 1401, Alcohols II, NIOSH Manual of Analytical Methods, Fourth Edition, (August 15, 1994).

18.13 NIOSH Method 1402, Alcohols III, NIOSH Manual of Analytical Methods,

Fourth Edition, (August 15, 1994).

18.14 NIOSH: Method 1403, Alcohols IV, NIOSH Manual of Analytical Methods, Fourth Edition, (March 15, 2003).

18.15 U.S. EPA Method 8240B, Revision 2, September 1994, Final Update IIA to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), EPA publication SW-846.

19 APPENDICES

Appendix 1 (SAS07-A1): GC-FID method using a Mid-Polar column.

Appendix 2 (SAS07-A2): GC-FID method using a PEG column.

Appendix 3 (SAS07-A3): Target Compounds

Appendix 4 (SAS07-A4): 80 mg/mL Stock Standards

Appendix 5 (SAS07-A5): 100 mg/mL Stock Standards

Appendix 1

SAS07-A1

GC-FID method using a Mid-Polar column.

Note – These data acquisition parameters are specific to CARB's use of an Agilent GC-FID: ACETONE, DCM, 1,1,1-TRICHLOROETHANE, MEK, SILOX, HEXGLY, TCE, and PDCB.

Any deviations will be documented with management approval.

ALS	
Syringe Size	10 µL
Injection Volume	1 µL
Inlet	
Heater	250°C
Inlet Mode	Split
Split Ratio	40:1
Septum Purge Flow	3.0 mL/min (default)
Column	
Mode	Constant Flow
Flow Rate	1.9 mL/min
Oven	
Initial Oven Temperature	40°C
Initial Time	6.0 min
Ramp 1 Rate	10.0°C/min
Ramp 1 Final Temperature	200°C
Ramp 1 Hold Time	1.0 min
Maximum Oven Temperature	240°C
Run Time	23.0 min
Oven Equilibration	0.30 min
Post-Temp & Time	40°C; 0.00 min
Detector / FID	
Heater	250°C
Hydrogen Flow	30.0 mL/min
Air Flow	400.0 mL/min
Mode	Constant Makeup + Fuel Flow
Makeup Flow	25.0 mL/min
Data Rate / Peak Width	20.00 Hz / 0.01 min

Appendix 2

SAS07-A2

GC-FID method using a PEG column.

Note – These data acquisition parameters are specific to CARB's use of an Agilent GC-FID: PEGLYCOL, CBPGLY, and DIPROP.

Any deviations will be documented with management approval.

ALS	
Syringe Size	10 µL
Injection Volume	1 µL
Inlet	
Heater	220°C
Inlet Mode	Split
Split Ratio	12:1
Column	
Mode	Constant Flow
Flow Rate	5.9 mL/min
Oven	
Initial Oven Temperature	80°C
Initial Time	2.0 min
Ramp 1 Rate	6.0°C/min
Ramp 1 Final Temperature	150°C
Ramp 1 Hold time	2.0 min
Ramp 2 Rate	20°C/min
Ramp 2 Final Temperature	220°C
Ramp 2 Hold Time	1.0 min
Maximum Oven Temperature	240°C
Run Time	20.17 min
Oven Equilibration	0.3 min
Post-Temp & Time	80°C; 0.00min
Detector / FID	
Heater	250°C
Hydrogen Flow	35.0 mL/min
Air Flow	400.0 mL/min
Mode	Constant Makeup Flow
Makeup Flow	25.0 mL/min
Data Rate / Peak Width	20.00 Hz / 0.01 min

Appendix 3

SAS07-A3

Target Compounds

Compounds
methanol
ethanol
acetone
isopropanol
methyl acetate
1-propanol
isobutanol
PERC
limonene
DCM
ethyl acetate
toluene
ethyl benzene
m-xylene
o-xylene
pinene
1,1,1-trichloroethane
p-chlorobenzotrifluoride
methyl ethyl ketone
PM acetate
2-butoxyethanol
HMDS
HMCTS
OMTS
OMCTS
DMTS
benzyl alcohol
DMCPS
AMP
hexylene glycol
propylene glycol
ethylene glycol
carbitol
butyl carbitol
propylene carbonate
dipropylene glycol

Appendix 4

SAS07-A4

80 mg/mL Stock Standards

GC Method Name	Calibration Standard Stock 80 mg/mL		Control/Check Standard Stock 250 mg/mL
ACETONE	methanol ethanol acetone isopropanol methyl acetate	1-propanol isobutanol PERC limonene	acetone water
DCM	DCM ethyl acetate toluene	m-xylene o-xylene pinene ethyl benzene	dichloromethane MEK
1,1,1-TRICHLOROETHANE	1,1,1-trichloroethane		1,1,1-trichloroethane
MEK	p-chlorobenzotrifluoride methyl ethyl ketone	2-butoxyethanol PM acetate	dichloromethane methyl ethyl ketone
SILOX	HMDS HMCTS OMTS OMCTS	DMTS benzyl alcohol DMCPS	hexamethyldisiloxane
HEXGLY	AMP	hexylene glycol	hexylene glycol
PEGLYCOL	propylene glycol	ethylene glycol	propylene glycol
CBPGLY	carbitol butyl carbitol	propylene carbonate	butyl carbitol
DIPROP	dipropylene glycol		dipropylene glycol

Appendix 5

SAS07-A5

100 mg/mL Stock Standards

GC Method Name	Calibration Standard Stock 100 mg/mL	Control/Check Standard Stock 250 mg/mL
TCE	trichloroethylene	trichloroethylene
PDCB	paradichlorobenzene	paradichlorobenzene