To: Michael Werst, Chief, Northern Laboratory Branch

From: Manisha Singh, Ph.D., Chief, Quality Management Branch

Date: August 23, 2024

Subject: Approval of Addendum to Standard Operating Procedure for the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography

Thank you for the submission of the Addendum to the Standard Operating Procedure (SOP) for Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography (SAS09, Revision 1.5). The Quality Management Section has reviewed the addendum along with the SOP and associated Addendum A47 (May 2024) and determined that it covers all required elements. The addendum is approved and has been assigned addendum number A50.

Please direct any comments or questions to Grace Tuazon at grace.tuazon@arb.ca.gov or (279) 208-7464.

Attachment

cc: Keith Kennedy, Manager, Special Analyses Section

Melissa Niederreiter, Manager, Quality Management Section

Jeff Wright, Manager, Laboratory Support Section

Grace Tuazon, Air Pollution Specialist, Quality Management Section

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		
District Name:	Northern Laboratory Branch Monitoring and Laboratory Division	
District Address:	1900 14th Street, Sacramento	
District Contact Name/Phone Number:	Keith Kennedy	916-322-2496
District Signature/Date:	Keith Kennedy	08/08/2024

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 the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography SAS09 Revision 1.5 with Addendum A47	February 9, 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).

Current Language (SOP Page 8 Section 9.1.11):
Verify that no more than two sample peaks with area counts greater than 1500 are present in the solvent blank chromatograms. If interfering peaks occur, stop the sequence, and bake out the system.

Proposed Language (SOP Page 8 Section 9.1.11):
Verify the solvent blanks meets the criteria described in section 10.1 (Quality Control).

Current Language (SOP Page 14 Section 10.2):
Method detection limit verifications are not applicable to this method. In simulated distillation, the calibration standard establishes the retention times of hydrocarbons ranging from C6 to C44 covering the boiling point range in the sample. The simulated distillation software limits the evaluation of the sample to peaks with areas greater than 1500.

Proposed Language (SOP Page 14 Section 10.2):
Method detection limit verifications are not applicable to this method. In simulated distillation, the calibration standard establishes the retention times of hydrocarbons ranging from C6 to C44 covering the boiling point range in the sample. The simulated distillation software limits the evaluation of the sample to peaks with a signal-to-noise ratio greater than 5.

Section 5. Justification for Deviation(s)
(provide explanation of why modification(s) to existing ARB document is necessary)

The changes above reflect:

- Clarification and correction of some points that were inadvertently not included in addendum A47.

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:	*manisha singh*	8/23/2024
Addendum Number	A50	

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

To: Michael Werst, Chief, Northern Laboratory Branch

From: Manisha Singh, Ph.D., Chief, Quality Management Branch

Date: May 24, 2024

Subject: Approval of Addendum to Standard Operating Procedure for the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography

Thank you for the submission of the Addendum to the Standard Operating Procedure (SOP) for Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography (SAS09, Revision 1.5). The Quality Management Section has reviewed the addendum along with the SOP and determined that it covers all required elements. The addendum is approved and has been assigned addendum number A47.

Please direct any comments or questions to Grace Tuazon at grace.tuazon@arb.ca.gov or (279) 208-7464.

Attachment

cc: Keith Kennedy, Manager, Special Analyses Section

Melissa Niederreiter, Manager, Quality Management Section

Grace Tuazon, Air Pollution Specialist, Quality Management Section

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		
District Name:	Northern Laboratory Branch Monitoring and Laboratory Division	
District Address:	1900 14th Street, Sacramento	
District Contact Name/Phone Number:	Keith Kennedy	916-322-2496
District Signature/Date:		

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 the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography SAS09 Revision 1.5	February 9, 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).

Current Language (Page 3 Section 8.4):
GC Column, Capillary, 10.0 m, 0.53 mm id. 2.65 µ film Restek MXT-2887 or equivalent

Proposed Language (Page 3 Section 8.4):
Metal capillary column, such as a Restek MXT-2887 at 10.0 m x 0.53 mm id. x 2.65 µ film, or equivalent

Open tubular column, such as an HP-1 at 10.0 m x 0.53 mm id. x 2.65 µ film, or equivalent

Current Language (Page 11 Section 9.3.6):
Verify that no more than two sample peaks with area counts greater than 1500 are present in the solvent blank chromatograms. If interfering peaks occur, stop the sequence, and bake out the system.

Proposed Language (Page 11 Section 9.3.6):
Verify the solvent blanks meet the criteria described in section 10.1 (Quality Control).

Current Section 10.1 (Table of Quality Controls):

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Solvent Blank	At the beginning of the sequence, following the calibration standard, following the reference oil, and before the control and each check	No more than two sample peaks with area counts greater than 1500 can be present in the solvent blank	If more than two sample peaks or a peak with an area count exceeding 1500 are present, bake the system out for at least two hours.

Proposed Section 10.1 (Table of Quality Controls):

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Solvent Blank	At the beginning of the sequence, following the calibration standard, following the reference oil, and before the control and each check	Peaks present in the C6-C44 retention times shall not have a signal-to-noise ratio greater than 5.	If the blank contains peaks identified in the C6-C44 retention times exceeding the maximum signal-to-noise the results are invalidated and samples must be reanalyzed.

Section 5. Justification for Deviation(s) *(provide explanation of why modification(s) to existing ARB document is necessary)*
The changes above reflect: • Equipment clarification to promote future optimized laboratory productivity. • Clarification and correction of some 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, Ph.D.	279-208-7896
Title:	Chief, Quality Management Branch	
Signature/Date:		5/24/2024
Addendum Number	A47	

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

Standard Operating Procedure for the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography

SAS09
Revision 1.5

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph.D., Chief Quality Management Branch	2/9/2022
Jeff Wright for Michael Werst Michael Werst, Chief Northern Laboratory Branch	2/9/2022

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 the Determination of Boiling Point Distribution in Consumer Products Using Gas Chromatography

1 Introduction

This document describes a procedure for the determination of the boiling point range in a consumer product to identify low vapor pressure-volatile organic compound (LVP-VOC) components under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 and 2, Section 94510(d). The Regulation states that compounds having an initial boiling point greater than 216 ºC are exempt from the definition of volatile organic compounds (VOC). The chromatographic conditions for this procedure are based on ASTM D 2887-01, "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography".

2 Summary of Method

SOP SAS09 measures exempt low vapor pressure-volatile organic compounds (LVP-VOC) in hydrocarbon based consumer products by simulated distillation gas chromatography/FID. The system is calibrated using an accurately weighed mixture of n-hydrocarbons (C6-C44) dissolved in a known amount of carbon disulfide (CS_2). The system efficiency is checked using a reference oil of known composition. Depending on the sample matrix, the sample can be analyzed neat or can be dissolved in CS_2 prior to analysis. The portion of the mass eluting after the retention time corresponding to a boiling point of 216 ºC and above is exempt from the definition of VOC in consumer products.

3 Acronyms and Definitions

Acronym or 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
ASTM	American Society for Testing and Materials
CARB	California Air Resources Board
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.
°C	Degrees Celsius
CS_2	Carbon Disulfide

Acronym or Term	Definition
FID	Flame Ionization Detector used in gas chromatography
GC	Gas Chromatograph
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
LVP	Low Vapor Pressure
LVP-VOC	Low Vapor Pressure-Volatile Organic Compounds
µl	Microliter
µ	Micron
m	Meter
mg	Milligram
min	Minutes
mL	Milliliter
mm	Millimeter
NLB	Northern Laboratory Branch
psi	Pounds per square inch
QC	Quality Control
QCM	Quality Control Manual
RPD	Relative Percent Difference
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 or any archive aliquot undergoing a re-test
sample dilution	Dilution made from the sample aliquot.
solvent blank	A sample consisting of the reagent used in the sample dilutions without the target compounds analyzed to determine interferences or contamination during analysis
SOP	Standard Operating Procedure
system blank	Solvent used to provide a profile of the baseline rise that occurs during instrument temperature programming. This profile is used to correct baseline drift during analysis of diluted samples
VOC	Volatile Organic Compound(s)

4 Interferences/Limitations

4.1 The procedure is limited to the analysis of products containing paraffinic, isoparaffinic, and/or hydrocarbon mixtures.

4.2 Carbon disulfide (CS_2) can cause baseline drift during analysis. The simulated distillation software subtracts a system blank of carbon disulfide from diluted samples to ensure proper baseline correction.

5 Personnel Qualifications

5.1 Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

5.2 Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

5.3 Training will be documented and maintained by the laboratory supervisor.

6 Safety Requirements

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

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

6.3 Ensure engineering controls are in place and operating (i.e., adequate ventilation).

7 Hazardous Waste

7.1 Discard used GC vials in the "Consumer Products GC Vial Waste" container located in the satellite hazardous waste accumulation area. Dispose the container contents in accordance with NLB's Chemical Hygiene Plan.

7.2 Discard autosampler rinse waste into the "Waste Consumer Products" container located in the satellite hazardous waste accumulation area. Dispose the container contents in accordance with NLB's Chemical Hygiene Plan.

8 Equipment, Supplies, and Chemicals

8.1 Balance, capable of accurately weighing to 0.1 mg

8.2 Pipettors, 250 µL and 2.5 mL with tips

8.3 Gas Chromatograph (GC) configured with a Flame Ionization Detector (FID) and autosampler

8.4 GC Column, Capillary, 10.0 m, 0.53 mm id. 2.65 µ film Restek MXT-2887 or equivalent

8.5 System Computer for GC equipment

8.6 Simulated distillation software used for automatic baseline correction of diluted samples and data analysis

8.7 Laboratory Information Management System (LIMS)

8.8 Helium, Grade 5

8.9 Hydrogen Generator capable of 80 psi output

8.10 Deionized water, ASTM Type 1

8.11 Air, compressed, ultra-high purity

8.12 Carbon Disulfide (CS_2), ACS grade or better

8.13 Undecane, ACS grade or better

8.14 Tridecane, ACS grade or better

8.15 Quantitative Calibration Mix, ASTM D 2887 Quantitative Calibration Mix (e.g., Supelco ASTM D2887, or equivalent.)

8.15.1 Store the calibration mix in the standards refrigerator.

8.16 Reference oil, ASTM D 2887 Reference Gas Oil (e.g., Supelco ASTM D2887 Reference Gas Oil, or equivalent.)

8.16.1 Store the reference oil in the standards refrigerator.

8.17 Control/Check Standard Stock is a 50%/50% mixture of Undecane and Tridecane:

8.17.1 Control/Check standard stock may be prepared from reagents or purchased as certified solutions. Prepare or procure a sufficient volume of control/check standards to use in several analyses. Store control/check standards in the standards refrigerator.

8.18 Laboratory vented enclosure

8.19 Standards Refrigerator, capable of maintaining a temperature range between 0 and 10 °C.

8.20 Pasteur pipettes, disposable with bulbs

8.21 Transfer pipettes, disposable

8.22 8mL screw top vials with cap

8.23 250 µL vial inserts

8.24 2 mL autosampler vials with caps

8.25 Autosampler vial cap crimper

8.26 Autosampler vial cap decrimper

9 Procedure

9.1 Annual calibration

9.1.1 Prepare new calibration standard.

9.1.1.1 Verify the analytical balance control has been completed. If not, complete the analytical balance control as described in SAS14.

9.1.1.2 Remove one 1-mL amber ampoule of Quantitative Calibration Mix from the standards refrigerator and let come to room temperature to ensure the calibration mix is completely liquefied.

9.1.1.3 Transfer the label from the amber ampoule of the Quantitative Calibration Mix onto an 8 mL screw top vial. Write the date and analyst initials on the 8 mL vial. Tare the 8 mL screw top vial on the balance in a vented enclosure.

9.1.1.4 Record the date prepared and the analyst preparing the calibration standard in LIMS at the Calibration Information link (see LIMS Manual: LVP 2887 Analysis).

9.1.1.5 Transfer the contents of the Quantitative Calibration Mix ampoule into the tared 8 mL vial, cap, and place on the balance.

9.1.1.6 Record the weight of the Quantitative Calibration Mix in LIMS at the Calibration Information link (see LIMS Manual: LVP 2887 Analysis).

9.1.1.7 Tare the balance with the capped 8 mL vial containing the Quantitative Calibration Mix. Add carbon disulfide to the 8 mL vial at approximately five times the weight of the Quantitative Calibration Mix and cap.

9.1.1.8 Record the weight of the carbon disulfide (solvent weight) in LIMS at the Calibration Information link (see LIMS Manual: LVP 2887 Analysis).

9.1.1.9 Combine the carbon disulfide and the Quantitative Calibration Mix. Store the calibration standard solution in the refrigerator for future use.

9.1.2 Verify Helium and Air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

9.1.3 Verify the deionized water in hydrogen generator reservoir is above the refill level. Add more deionized water to the reservoir as necessary prior to analysis.

9.1.4 Prepare the autosampler: Fill solvent rinse vial A with carbon disulfide and ensure that the rinse waste vials are empty.

9.1.5 Load the d2887a method and verify the conditions in the GC software as specified:

Initial Oven Temperature	40°C
Initial Time	0.00 min
Rate	15°/minute to 350° C
Final Temperature	350°C
Final Time	8.00 min
Injector Temperature	350°C
Detector Temperature	360°C
Hydrogen Flow	40.0 mL/min
Air Flow	450.0 mL/min
Makeup Flow	32.0 mL/min
Data Rate	10.00 Hz
Peak Width	0.02 min
Column Flow Rate	8.6 mL/min
Column Mode	constant flow

9.1.6 Load the CALIB sequence

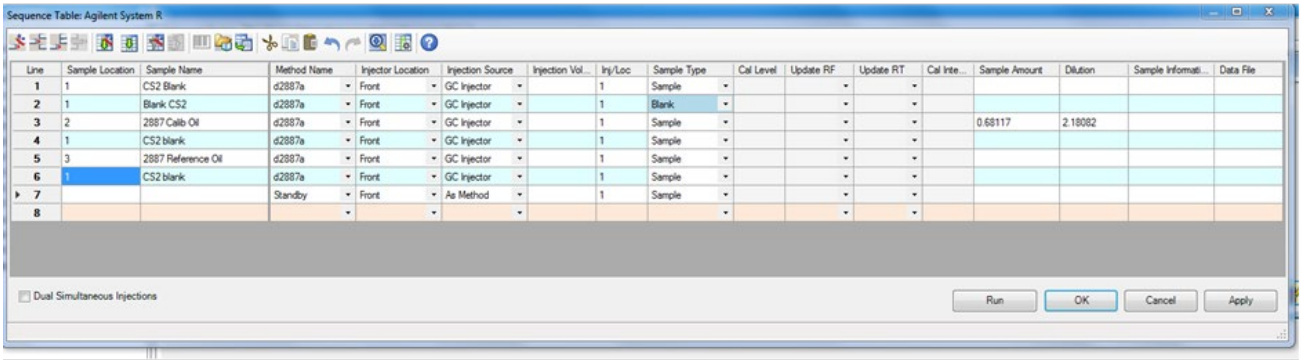
9.1.6.1 Edit Parameters

9.1.6.2 Enter your initials and the subdirectory for the data by editing the Sequence Parameters. The naming convention used for the subdirectory is month, day, year of analysis, and “C” (e.g., MMDDYYC).

9.1.6.3 A message “The directory or Subdirectory does not exist, do you want to create it?” should appear. Click on the Yes button. If the message does not appear, the directory already exists and will need to be modified. A letter or initials can be added to an existing subdirectory to uniquely identify samples analyzed on the same day.

9.1.6.4 Edit the Sequence table. See Figure 1 for representative sequence table.

Figure 1



9.1.6.4.1 The **Sample Location** column shall have vial numbers corresponding to the position on the autosampler tray. Each vial will have its own vial number.

9.1.6.4.2 In the **Sample Name** column, enter the samples to be analyzed. The following sequence should be followed for calibration:

Solvent Blank
System Blank
Calibration standard
Solvent Blank
Reference oil
Solvent Blank
Control/Check Standard

9.1.6.4.3 Ensure that the correct method is listed in the **Method Name** for all analyses. Add an additional line with the method STANDBY at the end of the sequence.

9.1.6.4.4 In the **Injector Location** column, confirm the location is set to Front for all analyses.

9.1.6.4.5 The **Injector Source** is set to GC Injector for all analytical runs. The injector source is set to As Method in the last line of the sequence.

9.1.6.4.6 The **Inj/Loc** column refers to the number of injections and should be “1” for all analyses.

9.1.6.4.7 **Sample Type** is Blank for the system blank and Sample for all others.

9.1.6.4.8 In the **Sample Amount** column, enter the weight of the Quantitative Calibration Mix from LIMS as described in 9.1.1.6.

9.1.6.4.9 In the **Dilution** column, enter the weight of the carbon disulfide from

LIMS as described in 9.1.1.8.

9.1.6.4.10 Check that all other columns are blank.

9.1.6.4.11 Click on OK when done and save the sequence.

9.1.6.4.12 Print the sequence by clicking on Sequence and then Print Sequence.

9.1.7 Transfer carbon disulfide to an appropriately labeled 2 mL autosampler vial and cap.

9.1.8 Transfer the prepared calibration standard and the reference oil to appropriately labeled 2 mL autosampler vials and cap.

9.1.9 Place the vials in the autosampler, matching the vial location in the sequence.

9.1.10 Run the sequence.

9.1.11 Verify that no more than two sample peaks with area counts greater than 1500 are present in the solvent blank chromatograms. If interfering peaks occur, stop the sequence, and bake out the system.

9.1.11.1 Load the BAKEOUT method.

9.1.11.2 Verify that the oven temperature reaches 350 °C. Run the BAKEOUT method for at least 2 hours.

9.1.11.3 Run the sequence again, repeating the BAKEOUT method if interfering peaks continue. Repeat until the criteria established in section 9.1.11 is met. If repeating the BAKEOUT method does not resolve interfering peaks in the solvent blank chromatogram, perform GC maintenance and/or call for instrument service.

9.1.12 Compare the calibration chromatogram portion of the report to the last saved calibration chromatogram to verify that all peaks are identified. All boiling point distribution peaks from C6 to C44 must be identified in the same order as the last saved successful calibration. If necessary, open the data analysis software to adjust the retention time(s) for unidentified peaks to ensure that all peaks are identified. Save changes to the chromatogram.

9.1.13 Evaluate the reference oil report to verify that the boiling point fractions are within the target boiling point ASTM D2887 Reference Oil Control Limits posted at or near the instrument as indicated in the reference oil certificate of analysis. The ASTM D2887 Reference Oil Control Limits are also located in the Consumer Products Reports LIMS application at the Control Limits link. If any of the boiling points are not within the ASTM D2887 Reference Oil Control Limits, reanalyze the entire calibration sequence. Perform GC maintenance as needed prior to reanalysis.

9.2 Sample Analysis Preparation

9.2.1 Verify Helium and Air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

9.2.2 Verify the deionized water in hydrogen generator reservoir is above the refill level. Add more deionized water to the reservoir as necessary prior to analysis.

9.2.3 Prepare the autosampler: Fill solvent rinse vial A with carbon disulfide and ensure that the rinse waste vials are empty.

9.2.4 Load the d2887a method and verify the conditions in the GC software as specified:

Initial Oven Temperature	40°C
Initial Time	0.00 min
Rate	15°/minute to 350° C
Final Temperature	350°C
Final Time	8.00 min
Injector Temperature	350°C
Detector Temperature	360°C
Hydrogen Flow	40.0 mL/min
Air Flow	450.0 mL/min
Makeup Flow	32.0 mL/min
Data Rate	10.00 Hz
Peak Width	0.02 min
Column Flow Rate	8.6 mL/min
Column Mode	constant flow

9.2.5 Load the D2887A sequence

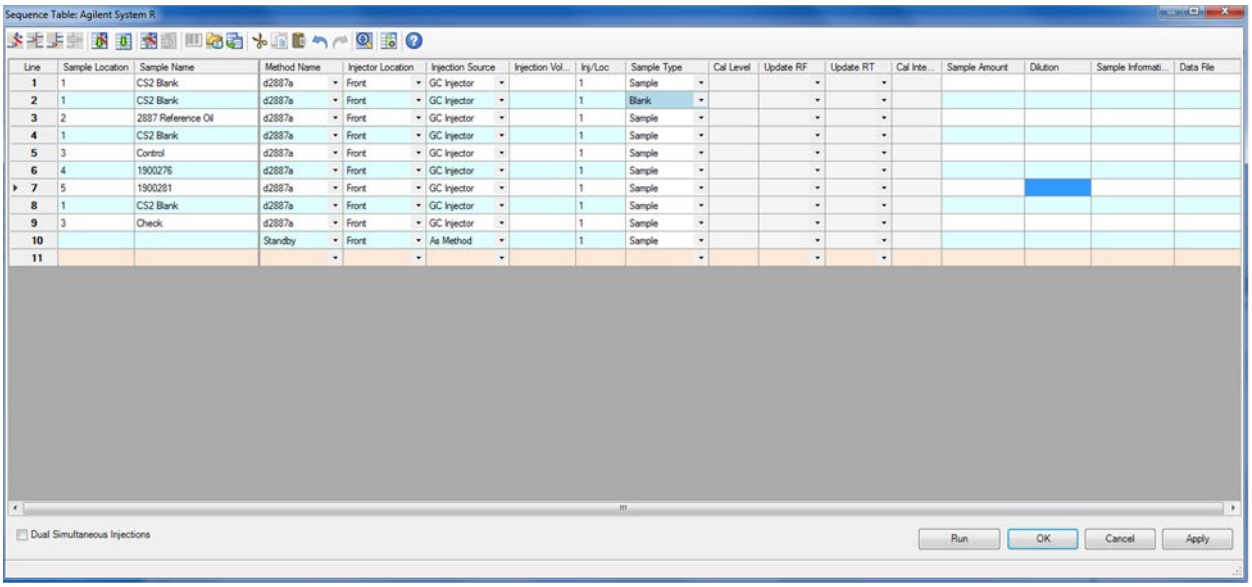
9.2.5.1 Edit Parameters

9.2.5.2 Enter your initials and the subdirectory for the data by editing the Sequence Parameters. The naming convention used for the subdirectory is month, day, and year of analysis (e.g., MMDDYY).

9.2.5.3 A message “The directory or Subdirectory does not exist, do you want to create it?” should appear. Click on the Yes button. If the message does not appear, the directory already exists and will need to be modified. A letter or initials can be added to an existing subdirectory to uniquely identify samples analyzed on the same day.

9.2.5.4 Edit the Sequence table. See Figure 2 for representative sequence table.

Figure 2



9.2.5.4.1 The **Sample Location** column shall have vial numbers corresponding to the position on the autosampler tray. Each vial will have its own vial number.

9.2.5.4.2 In the **Sample Name** column, enter the samples to be analyzed. The following sequence should be followed for sample analysis:

Solvent Blank
System Blank
Reference oil
Solvent Blank
Control Standard
Sample aliquots
Solvent Blank
Check Standard

9.2.5.4.2.1 The system blank is only required when samples are diluted in carbon disulfide.

9.2.5.4.3 Ensure that the correct method is listed in the **Method Name** for all analyses. Add an additional line with the method STANDBY at the end of the sequence.

9.2.5.4.4 In the **Injector Location** column, confirm the location is set to Front for all analyses.

9.2.5.4.5 The **Injector Source** is set to GC Injector for all analytical runs. The

injector source is set to As Method in the last line of the sequence.

9.2.5.4.6 The **Inj/Vial** column refers to the number of injections and should be "1" for all analyses.

9.2.5.4.7 **Sample Type** is Blank for the second system blank (used for diluted samples) and Sample for all others.

9.2.5.4.8 Check that all other columns are blank.

9.2.5.4.9 Click on OK when done and save the sequence.

9.2.5.4.10 Print the sequence by clicking on Sequence and then Print Sequence

9.3 Analysis Preparation

9.3.1 Prepare the analytical batch for the analysis by transferring sample aliquots prepared in SOP SAS14 to new 2 mL autosampler vials and cap.

9.3.1.1 If a sample aliquot is viscous or a solid, place approximately 0.25 mL of sample aliquot into a new 2 mL autosampler vial. Add approximately 1.4 mL of carbon disulfide. Cap and mix well.

9.3.2 Transfer carbon disulfide to an appropriately labeled 2 mL autosampler vial and cap.

9.3.3 Transfer the reference oil and control/check standards to appropriately labeled 2 mL autosampler vials and cap.

9.3.4 Place the vials in the autosampler, matching the vial location in the sequence.

9.3.5 Run the sequence.

9.3.6 Verify that no more than two sample peaks with area counts greater than 1500 are present in the solvent blank chromatograms. If interfering peaks occur, stop the sequence, and bake out the system.

9.3.6.1 Load the BAKEOUT method.

9.3.6.2 Verify that the oven temperature reaches 350 °C. Run the BAKEOUT method for at least 2 hours.

9.3.6.3 Run the sequence again, repeating the BAKEOUT method if interfering peaks continue. Repeat until the criteria established in section 9.3.6 is met. If repeating the BAKEOUT method does not resolve interfering peaks in the solvent blank report chromatogram, perform GC maintenance and/or call for instrument service.

9.3.7 Evaluate the reference oil report to verify that the boiling point fractions are within the target boiling point ASTM D2887 Reference Oil Control Limits posted at or near the instrument as indicated in the reference oil certificate of analysis. The ASTM D2887 Reference Oil Control Limits are also located in the Consumer Products Reports LIMS application at the Control Limits link. If any of the boiling points are not within the ASTM D2887 Reference Oil Control Limits, repeat analysis of the reference oil. If samples are affected, repeat the sequence. Perform GC maintenance or recalibrate as needed prior to reanalysis.

9.3.8 Review the control/check standard report to verify that the control/check standard recoveries are within the control limits posted at or near the instrument. The control limits are also located in the Consumer Products Reports LIMS application at the Control Limits link. If any of the control/check standards are not within the control limits, reanalyze the affected samples. Perform GC maintenance or recalibrate as needed prior to reanalysis.

9.3.9 Any anomalies occurring during the analysis that affect the data shall be documented, the affected data invalidated, and all affected samples shall be reanalyzed. If anomalies continue, notify management and proceed under their direction.

9.3.10 Any instrument issues or maintenance shall be documented in the instrument logbook to be kept with the instrumentation at all times.

9.3.11 Upload valid data to LIMS (see LIMS Manual: LVP 2887 Analysis).

9.3.12 After sequence completion, remove 2 mL autosampler vials from the autosampler, and ensure the instrument has the STANDBY method loaded.

10 Quality Control

10.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Solvent Blank	At the beginning of the sequence, following the calibration standard, following the reference oil, and before the control and each check	No more than two sample peaks with area counts greater than 1500 can be present in the solvent blank	If more than two sample peaks or a peak with an area count exceeding 1500 are present, bake the system out for at least two hours.
Calibration	Annually	All boiling point distribution peaks from C6 to C44 must be identified in the same elution order as the last successful calibration retention times	If any peak(s) are not identified, label the unidentified peaks in the simulated distillation software.
Reference Oil	After the second solvent blank in the calibration sequence, after the system blank in the sample sequence	The boiling point temperature ranges must be within ASTM D2887 Reference Oil Control Limits stated on the Certificate of Analysis.	If any boiling point range is outside the limits, reanalyze the reference oil and any affected samples.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Control/Check Standard	The control is analyzed after the reference oil, and the checks after every ten or less samples and at the end of the analytical sequence.	Warning and control limits are set at ±8 and ±10 percent respectively from the target value	If an analysis is out of the control limits, the affected sample result(s) are invalid. Take action to bring the system back into control and reanalyze the control/check standard and any samples not bracketed by successful control/check standards. 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	Re-analyze replicate pair. If criteria not met after subsequent re-analysis, or if re-analysis is not possible, analytical result for that replicate pair will be invalidated.
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.

10.2 Method detection limit verifications are not applicable to this method. In simulated distillation, the calibration standard establishes the retention times of hydrocarbons ranging from C6 to C44 covering the boiling point range in the sample. The simulated distillation software limits the evaluation of the sample to peaks with areas greater than 1500.

10.3 Equipment Requirements

10.3.1 The balance used requires calibration by an outside source annually.

10.3.2 Pipettors require certification by an outside source annually.

11 Sample and Data Management

11.1 Data management consists of samples logged into the 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 kept with the instrumentation at all times.

11.2 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.

12 Calculations

12.1 The percent LVP-VOC is calculated as:

$$\text{Percent LVP-VOC} = 100 - \text{percent mass recovered}$$

Where:

percent mass recovered = the portion of the mass eluting after the retention time corresponding to a boiling point of 216 ºC

12.1.1 In the sample boiling point distribution list, find the first boiling point that is greater than 216 °C.

12.1.2 Note the corresponding percent mass recovered.

12.2 Relative Percent Difference (RPD)

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

Where:

X = the sample result

Y = the duplicate result

13 References

13.1 Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds (ROC) in Aerosol Coating Products, May 25, 2018 https://www.arb.ca.gov/regact/2018/cp2018/method310.pdf

13.2 Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 and 2, Section 94510(d)

13.3 ASTM D 2887-01 Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, 2001

13.4 NLB Laboratory Quality Control Manual, Revision 4.0, September 17, 2018

13.5 SOP MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 0.0, July 18, 2017

13.6 NLB Chemical Hygiene Plan, June 2019 (or most current version)

13.7 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS), October 15, 2019

13.8 SOP SAS14 Standard Operating Procedure for Consumer Product Sample Preparation, Revision 0.0, August 5, 2019

14 SOP Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** Revision 1.0		
	December 1, 1997	Reference to the new 6890 and updated AC SimDist software. Changes in sample preparation.	Unknown
2	**Description:** Revision 2.0		
	June 10, 1998	Method is referenced as an additional procedure for VOC analysis, LVP-VOC if suspect in a consumer product.	Unknown
3	**Description:** Revision 1.3		
	December 10, 2009	Added Appendix A and renumbered to new section number.	Unknown

	Date	Updated Revision	Original Procedure
4	**Description:** Revision 1.4		
	August 17, 2010	Edited and removed references to weight for reference oil, or sample preparation prior to analysis.	Unknown
5	**Description:** Revision 1.5		
	February 9, 2022	Reviewed for grammar and content, and compliance with the most recent versions of the QC Manual and MLD076 Revision 0.0. Miscellaneous additions/deletions made. Incorporated APPENDIX A into body of SOP. Added additional QC: control/check	Editorial and administrative changes. Original procedure did not have the control/check criteria.