

California Environmental Protection Agency



Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS09

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

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DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by ARB laboratory. Any functionally equivalent instrumentation can be used.

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 °C 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 (CS₂).

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 CS₂ prior to analysis. The portion of the mass eluting after the retention time corresponding to a boiling point of 216 °C is exempt from the definition of VOC in consumer products.

3 INTERFERENCES/LIMITATIONS

- 3.1 The procedure, at this time, is limited to the analysis of paraffinic/isoparaffinic mixtures. Work is in progress to adapt this procedure to hydrocarbon mixtures containing aromatic, olefinic, and alkyl acetate compounds.
- 3.2 A blank analysis (neat CS₂) must be subtracted from the sample analyses to insure proper baseline correction.

4 APPARATUS AND MATERIALS

- 4.1 Balance: capable of accurately weighing to 0.1 mg.
- 4.2 Positive displacement pipettor, 250 µL and 2.5 mL.
- 4.3 Gas chromatographic system equivalent to Agilent Model 6850/Chemstation equipped with an FID and a 10.0 m, 0.53 mm id. 2.65 µ film Restek MXT-2887 capillary column.

4.4 Simulated distillation software from Analytical Controls Version 03.04/04.09.01 (or other vendor), is used for automatic baseline subtraction and calculation routines.

5 GASES AND REAGENTS

5.1 Helium: Grade 5 for gas chromatography.

5.2 Hydrogen: Grade 5 or Whatman Hydrogen generator.

5.3 Compressed Air, Purified.

5.4 Carbon Disulfide, Reagent Grade.

5.5 Calibration Standard: accurately weigh the contents of a 1 mL amber vial of ASTM D 2887 Quantitative Calibration Mixture (Supelco ASTM D2887, or equiv.) into a tared 8 mL vial. Record the weight of the calibration standard. Tare the 8 mL vial and add CS₂ to the dilution vial to make no more than a 5x dilution. Record the weight of the CS₂.

5.6 Reference Oil: Pipette 500 µL of Reference Gas Oil Sample (Supelco ASTM D2887 Reference Gas Oil, Lot, or equiv.) into a GC vial with a 500 µL glass insert. The reference oil is ready for analysis.

6 PROCEDURE

6.1 Set up the 6850 GC system to the following conditions:

Injector Temperature:	325 °C
Detector Temperature:	350 °C

Oven Temperature Program:

Initial:	40 °C
Initial rate:	15 °C /min to 350 °C
Injection:	Split
Column Flow Rate:	8.7 mL/min
Helium Makeup Flow to FID:	30.0 mL/min
Automatic Liquid Sampler, 1.0 µL injection volume	

6.2 Run reagent grade carbon disulfide. Record system background chromatogram. With the exception of the carbon disulfide, there should be no peaks in the

chromatogram. If interfering peaks appear, bake out the system until clean. Rerun CS₂ reagent blank.

- 6.3 Run the Calibration Standard. Check to insure that peak retention times are within 0.1 minute of previous calibrations. If not, manually input the new retention times for the C₆ to C₄₄ hydrocarbon peaks.
- 6.4 Run Reference Sample. The data system will automatically adjust the integrated areas for baseline and solvent peak areas. Make sure that the Target Value Boiling points are within five degrees (5°) of the Determined Values. If not, reevaluate the most recent calibration, and perform GC maintenance if required.
- 6.5 Pipette the liquid sample into a 1.8 mL amber vial. If the sample is viscous or a solid, dilute or dissolve the sample in approximately 1.4 mL of CS₂. Mix well and ensure that the resulting dilution is not biphasic and or the solid has completely dissolved. Inject 1.0 µL of diluted sample into GC system. Fraction of LVP-VOC is calculated as

$$\text{Fraction LVP-VOC} = \frac{\text{Integrated area of sample after retention time of 216 } ^\circ\text{C}}{\text{Total integrated area of chromatogram}}$$

Make sure to inspect the chromatogram to determine that the baseline at the end of the run has become steady. If not, additional material may not have eluted from the column under the analytical conditions. This would indicate that the sample is not suitable for this procedure. Analyze a solvent blank sample after any sample with more than 10% of the integrated area after n-C₃₆ to check for carry-over.

APPENDIX A

Preparation of Calibration Standard and Reference Oil Check

1 PREPARATION OF CALIBRATION STANDARD

- 1.1 Prepare new calibration oil solution, if necessary. If there is some calibration oil solution already prepared, fill a GC vial with this solution and proceed to step 2.
- 1.2 Remove one 1-mL amber vial of calibration oil (Supelco ASTM D2887 Quantitative Calibration Mix 1-12% wt./wt. or equivalent) from the refrigerator and let come to room temperature.
- 1.3 Transfer the label from the amber vial onto an 8 mL dilution vial. Write the date on the dilution vial. Tare the dilution vial on the balance in the vented enclosure. Transfer the calibration oil into the tared dilution vial and record the weight of the oil in the 2887 logbook.
- 1.4 Tare the dilution vial with the calibration oil. Add CS₂ to the dilution vial to make no more than a 5x dilution. Record the weight of the CS₂ (solvent weight) in the 2887 logbook.
- 1.5 Mix well the calibration oil and CS₂. Transfer some of the diluted calibration oil to a GC vial and cap. Store the remaining calibration oil solution in the refrigerator for future use.

2 PREPARATION OF REFERENCE OIL CHECK

- 2.1 To prepare the reference oil check, obtain Supelco ASTM D2887 Reference Gas Oil, Lot2, neat mix from the refrigerator. Let come to room temperature. Pipette 200 µL of the reference oil into a GC vial.
- 2.2 Add approximately 1.0 mL of CS₂ to the reference oil in the GC vial. Mix well.

3 GC CONDITIONS AND SETTINGS

- 3.1 Column: Restek MXT-2887, 10.0m, 0.53mm id, 2.65µm film.
- 3.2 Set up the 6850 GC system as described in section 6.1
- 3.3 Check that there is sufficient He (carrier gas) and compressed air for the run.

The tank(s) should be changed when the pressure regulator indicates 500 psi or

less. Also check the water level in the hydrogen generator.

- 3.4 Fill and cap a GC vial with CS₂. This will be your blank.
- 3.5 Place GC vials in the autosampler in the following order: position 1 - CS₂ blank, position 2 – calibration oil, position 3 – reference oil check.
- 3.6 Open GC Instrument 1 (online) window. At the view pull-down menu, select method/run control (1). To load the method, go to the method pull-down menu and select load method. Highlight and double click on **d2887a.m**. A window may appear saying the method has changed. Select “no” to any changes.
- 3.7 Go to view pull-down menu; select **Simdis** program window (4).
- 3.8 Go to the sequence pull-down menu; select open. A window may appear indicating that the sequence has changed. Select “no” to any changes. Select **calib.s** sequence. Click on OK. Go to sequence pull-down menu, select edit. Under data destination, enter the date of the analysis. At the table below sequence parameters, there are three lines for the calibration run. Line 1 is the CS₂ blank. Do not make any changes to this line. Line 2 is the calibration oil sample. If you made new calibration oil standard, change the sample weight and solvent weight. Otherwise make no changes, but confirm that the sample and solvent weights in the table are the same as the ones from the previous calibration recorded in the D2887 logbook. Line 3 is the Reference oil check. Select OK. A window should appear asking to create a new file for the data. Select “yes”. From the sequence pull down menu select print to print the sequence list.
- 3.9 Go to the run control pull-down menu; select run sequence.
- 3.10 After analysis, the GC should automatically go into standby mode. If it does not, go to the view pull-down menu; select method and run control. At the method pull-down menu, select **standby.m** method.

4 CALIBRATION REPORT

The analysis of the calibration oil produces a three page report consisting of:

- a chromatogram
- calibration report table
- boiling point vs. retention time plot

Check the boiling point vs. retention time plot to confirm the analysis resulted in a linear plot.

5 SAMPLE PREPARATION

Note: Use pure (undiluted) sample for this analysis if possible otherwise dilute into CS₂.

- 5.1 Prepare check: Use the reference oil prepared in Section 2.2 as the check.
- 5.2 Prepare samples: Aliquot approximately 1.8 mL of liquid sample into an amber vial. Viscous and solid samples should be dissolved in CS₂ prior to analysis.
- 5.3 Fill a GC vial with pure CS₂ as a blank.

6 HP 6850 GC INSTRUMENT SETUP FOR SAMPLES

- 6.1 Place samples in the autosampler in the following order: position 1: CS₂ blank, position 2: check (reference oil), position 3 – end: samples.
- 6.2 On the PC, the 6850 software should be open. Under the view pull-down menu, select method and run control. Go to the method pull-down menu; select load method. If a window appears indicating the method has changed, select “no” to any changes. Select **d2887a.m** method.
- 6.3 Go to the sequence pull-down menu; select load sequence. If a window appears indicating the sequence has changed, select “no” to any changes. Select **2887.s** sequence.
- 6.4 Go to the view pull-down menu; select **Simdis (4)**.
- 6.5 Go to the sequence pull-down menu, select edit. The sequence editor window will appear. Enter the analysis date under data destination (numeric month/day/year). The first two lines of the sequence table indicate the blank and reference oil check. At line 3 and each subsequent line, type in sample number under the name column. Under the sample type column, select **ASTM D2887 Sample**. Under the GC Method column, enter D2887A. Under the inj/vial column type in 1. Select OK. A window should appear asking to create a new file for the data. Select OK.
- 6.6 Go to the sequence pull-down menu; select print.
- 6.7 Go to the run control pull-down menu; select run sequence.
- 6.8 After analysis, the GC should automatically go into standby mode. If it does not, go to the view pull-down menu; select method and run control. At the method

pull-down menu, select **standby.m** method.

7 SAMPLE RESULTS

The 2887 method generates the following reports for each sample analyzed:

- boiling distribution list
- boiling distribution plot
- chromatogram

To determine % LVP in the sample:

- 7.1 Go to the boiling point distribution list. The list indicates % sample mass boiled at a given temperature as well as the initial boiling point (IBP) and final boiling point (FBP) of the sample.
- 7.2 The reference solvent dodecane boils at around 216 °C. Any sample mass that boils above 216 °C is considered LVP-VOC.
- 7.3 Find the % mass that boiled at 216 °C on the boiling point distribution list. Subtract this % mass from 100%. This equals the % LVP. In other words:

$$\% \text{ LVP} = 100\% - \% \text{ mass at } 216^\circ\text{C}.$$

(For example, 95% sample mass boiled at 216 °C. % LVP = 100% - % mass at 216 °C. Therefore, 100% - 95% = 5% LVP.)

- 7.4 Sometimes the % mass at 216 °C is not reported on the boiling point distribution list. In this case, select the lowest % mass at the temperature reported above 216 °C to determine % LVP. (For example, the boiling point may jump from 215.5 °C at 74% mass to 230°C at 75% mass. Calculate the % LVP using the 75% mass boiled at 230°C.)
- 7.5 Report the % LVP on the consumer products laboratory report sheet under ASTM 2887.

Revision History

DATE	VERSION	NOTES
December 1, 1997	1.0	Reference to the new 6890 and updated AC SimDist software. Changes in sample preparation.
June 10, 1998	2.0	Method is referenced as an additional procedure for VOC analysis, LVP-VOC if suspect in a consumer product.
December 10, 2009	1.3	Added Appendix A and renumbered to new section number.
August 17, 2010	1.4	Edited and removed references to weight for reference oil, or sample preparation prior to analysis.