Standard Operating Procedure for the Total Volatile Measurement of Consumer Products

SAS 01
Revision 2.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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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.

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Standard Operating Procedure for the Total Volatile Measurement of Consumer Products

1 Introduction

This standard operating procedure (SOP) describes a procedure for the measurement of the total volatile content in a non-aerosol sample or the non-propellant portion of an aerosol sample, following Method 310 as required by The California Consumer Products Regulations. This SOP is based on U.S. Environmental Protection Agency (U.S. EPA) Method 24/24A and American Society Testing and Materials (ASTM) D2369-97.

2 Summary of Method

Gravimetric analysis is for the determination of total volatile content in a sample. This procedure details the process for weighing a portion of the sample aliquot into a weighing dish and heating it in a forced-air oven at 110±5 degrees Celsius (°C) for one hour. The total volatile content is the difference in weight of the sample before and after heating.

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 Standards for Testing and Materials
Batch Sample (BS)	A laboratory prepared sample aliquot of known concentration for QC evaluation under Method 310
°C	Degrees Celsius
CARB	California Air Resources Board
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
g	Gram(s)
ID	Identification
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
mL	Milliliter

Acronym or Term	Definition
mm	Millimeter
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
QC	Quality Control
QCM	Quality Control Manual
replicate	An additional analysis of the same sample aliquot or sample dilution
RL	Reporting Limit
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, the Batch Sample, or any archive aliquot undergoing a re-test
sample batch	A set of samples analyzed together under Method 310
sd	Standard deviation
SOP	Standard Operating Procedure
VOC	Volatile Organic Compound(s)

4 Interferences

4.1 Certain consumer products may react with the aluminum weighing dishes. Observation of change in the appearance of the aluminum weighing dish or sample effervescence can be an indication of a reaction. In these cases, substitute with Teflon weighing dishes.

For example, sodium hydroxide is a common ingredient in oven cleaners and reacts with aluminum weighing dishes. If sodium hydroxide is a listed ingredient, then a Teflon weighing dish is used.

4.2 Samples with entrained propellant can forcibly eject residues in the oven. If this occurs, follow the procedure in APPENDIX A.

5 Personnel Qualifications and Training

5.1 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/or 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).

6.4 Use heat resistant gloves when handling hot items (e.g., removing items from the oven).

7 Hazardous Waste

There is no generation of hazardous waste by this method.

8 Equipment, Supplies, and Chemicals

8.1 Oven, forced draft, able to maintain a temperature of 110±5ºC (ASTM Type II A or Type II B recommended)

8.2 Laboratory vented enclosure

8.3 Analytical Balance, capacity of at least 200g x 0.00001g readability (e.g., Mettler XP205)

8.4 Balance weighing basket or small beaker (e.g., 50mL)

8.5 1g Mass, ASTM class 1 or better

8.6 Laboratory workstation for analytical balance

8.7 Software for data transfer and collection (e.g., BalanceTalk, Excel, LabX)

8.8 Laboratory Information Management System (LIMS)

8.9 Weighing Dishes

8.9.1 Aluminum Weighing Dishes with a smooth (planar) bottom surface (e.g., Aluminum Crinkle Dish with Tab, 57mm)

8.9.2 Teflon Weighing Dishes, approximately 50mm x 15mm with a smooth (planar) bottom surface

8.10 Syringe, disposable, 3-5mL, with caps

8.11 Transfer Tubes, disposable, 3-5mL capacity

8.12 Task wipes (e.g., Kimwipes)

8.13 Desiccator with hygrometer and desiccant

8.14 Vortex mixer (e.g., Vortex Genie 2)

8.15 Gloves, non-powdered nitrile or suitable alternative

8.16 Forceps

8.17 Tray, low-rimmed metal (e.g., “cookie sheet”)

8.18 Heat Resistant Gloves (e.g., oven mitt)

8.19 Clock or timer

8.20 Reagents and Samples

8.20.1 Acetone, ACS grade or better

8.20.2 Methanol, ACS grade or better

8.20.3 Sample Aliquots (SAS 14)

8.20.4 Oven Control, ASTM Type I water

9 Procedure

Note: For the analysis of dryer sheets, refer to APPENDIX B. Samples containing sodium hydroxide require the use of Teflon weighing dishes.

9.1 Enter the analytical batch in LIMS following procedures outlined in the LIMS Manual (see LIMS: Replicate Sample Generation). LIMS will randomly assign a replicate for the analytical batch.

9.2 Gloves shall be worn during all steps of this procedure to prevent weighing errors due to handling.

9.3 Label weighing dishes with unique identifiers using a permanent marker.

9.4 Place weighing dishes on the tray, and place in the oven for one hour at 110±5ºC.

9.5 Using heat resistant gloves, remove the tray from the oven and place weighing dishes in desiccator to cool to room temperature. Ensure the hygrometer reads “Low Humidity.”

9.5.1 If the desiccator hygrometer reads “High Humidity”, do not use. Recheck the hygrometer the following day and if it continues to read, “High Humidity”,

replace the desiccant.

9.6 Remove the weighing dishes from desiccator and place on the tray.

9.7 Ensure data transfer software is open on the laboratory workstation and follow the general sequence:

9.7.1 Balance Control (one time prior to weighing session)
9.7.2 Samples (including replicates and duplicates as indicated in section 10)
9.7.3 Oven Control (one per analytical batch)
9.7.4 Balance Check (one time after weighing session)

9.8 Ensure the accuracy of the analytical balance.

Perform a balance control on the analytical balance prior to use.

Using forceps, place a 1g mass on the analytical balance. When the reading becomes stable, as indicated by the analytical balance, record the weight in LIMS (refer to LIMS Manual: Gravimetric Analysis). If the weight is not within the control limits (±2sd of the target value as established per the QCM), re-weigh the mass and record in LIMS. If the weight is still outside the control limits, there may be a problem with the analytical balance or the mass. Contact appropriate personnel for service.

9.9 Open the data collection software located on the laboratory workstation desktop and enter the information for the analytical batch (refer to LIMS Manual: Gravimetric Analysis). Save spreadsheet under a naming system that includes the sample ID numbers.

9.10 Weigh the empty weighing dish and record the weight on the spreadsheet.

9.10.1 Place the cursor in the “Weight Pan (g)” column for the first sample.

9.10.2 Weigh the corresponding empty weighing dish to 0.00001g and transfer the weight value to the worksheet by pushing the transfer button on the analytical balance. The highlighted data input area should advance automatically to the next field. Alternatively, use the arrow keys to move to the next sample.

9.10.3 Repeat for all remaining weighing dishes in the analytical batch.

9.11 Weigh the sample aliquot and/or oven control and record the weight.

Viscous samples or other materials such as creams, pastes, gels, and semi-solids may require the use of a transfer tube in place of a syringe or dispensing into the weighing dish directly from the sample container. If a transfer tube is used, then the sample should be applied in as thin of a film as practicable to maximize surface area. As a final remedy, a small amount of methanol or acetone can assist in evenly distributing the sample over the bottom of the

weighing dish; however, use this methanol or acetone technique sparingly to minimize unintended chemical reactions that could affect the overall volatility of the neat sample.

9.11.1 Tare a clean beaker or balance weighing basket.

9.11.2 For each sample aliquot, mix to ensure homogeneity, vortexing if needed.

9.11.3 Using a syringe, draw up approximately 1-2mL. Wipe the sides of the syringe with a task wipe to remove any residual sample.

9.11.4 Cap and weigh the syringe with sample by placing it in the tared beaker or balance weighing basket. Transfer the weight to the column marked, “Syringe Weight (g) – Initial weight.”

9.11.5 Dispense approximately 1mL into the appropriately labeled weighing dish.

9.11.6 Cap and reweigh the syringe. Transfer the weight to the column marked, “Syringe Weight (g) – Final weight.” The difference, as computed on the “Grav Calc” worksheet, is the actual amount of the sample placed in the weighing dish.

9.11.7 Repeat sections 9.11.1 through 9.11.6 for all samples and oven control in the analytical batch.

Prepare the assigned replicate(s) by either repeating sections 9.11.1 through 9.11.6 from the same sample aliquot or use the remainder of the sample in the syringe.

9.12 Place the tray of weighing dishes with samples in the oven at 110±5ºC for one hour.

9.13 Using heat resistant gloves, remove the tray of weighing dishes from the oven and place weighing dishes in the desiccator to cool to room temperature for a minimum of five minutes.

9.14 Weigh the weighing dish with residue to the nearest 0.00001g and transfer the weight value to the “Weight Pan + Residue” column for each sample and oven control on “Grav Calc” worksheet. If the sample appears to be reacting with the aluminum weighing dish (i.e., effervescence, discoloration, etc.), repeat from section 9.1 for the affected sample using a Teflon weighing dish. Even when using Teflon weighing dishes, some samples can forcibly eject residue out of the dish. If there is evidence that this has occurred, utilize the procedure in APPENDIX A for the samples that ejected residue, and reanalyze the entire analytical batch.

9.15 The workbook will calculate the total weight percent of volatile content in the sample or oven control in accordance with section 12. For replicate results ≥ 5 x

RL, the RPD must be ≤ 25. If replicate criterion is not met, results are invalid. Reanalyze the analytical batch.

9.16 If the oven control results are not within acceptable values (±3sd of the target value as established per the QCM), check the balance and/or oven conditions and reanalyze the analytical batch.

9.17 Perform a Balance Check after all weighing is complete.

9.17.1 Using forceps place the 1g mass on the analytical balance. When the reading becomes stable as indicated by the analytical balance, record the weight in LIMS (see LIMS Manual: Gravimetric Analysis).

9.17.2 If the weight is not within Balance Check criteria, reanalyze the analytical batch.

9.18 Upload the data to LIMS (refer to LIMS Manual: Gravimetric Analysis).

10 Quality Control

10.1 Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Balance Control	Prior to weighing session	±2sd of the target value	If outside control criteria, re-weigh the 1g mass standard and record in LIMS. If the weight is still outside the control limits, there may be a problem with the balance or the mass. Notify management and contact appropriate personnel for service.
Balance Check	After weighing session	±2sd of the target value	If outside criteria, the entire analytical batch is invalid. Reanalyze the analytical batch. See corrective actions for Balance Control.
Oven Control	One per analytical batch	Total weight percent VOC within ±3sd of the target value	Perform a Balance Check. If the balance check is outside the control limits, perform corrective action for the balance check. If balance check is within control limits, check the oven conditions.

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
			Bring oven conditions back into control, contacting appropriate personnel for service if necessary. All samples are invalid. Reanalyze the analytical batch.
Replicate	One of ten or fewer samples in the analytical batch	For replicate results ≥ 5 x RL: RPD ≤ 25	Reanalyze the analytical batch. If criteria not met after subsequent re-analysis, or if re-analysis not possible, analytical results 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 Equipment Requirements

10.2.1 The analytical balance requires calibration by an outside source annually. Calibration check masses must be the appropriate ASTM International class.

10.2.2 The 1g mass is calibrated by an outside source annually and must be certified as traceable to NIST mass standards.

10.2.3 The oven requires verification by an outside source using NIST traceable test equipment 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 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 SAS 13 and SAS 14.

11.3 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.

12 Calculations

Note: Refer to APPENDIX B for calculations related to the analysis of dryer sheets.

12.1 Weight fraction of total volatile content in a non-aerosol sample or the non-propellant portion of an aerosol sample (per weighing dish)

$$TV = \frac{(B - C) - (D - A)}{(B - C)}$$

Where:

TV	=	Weight fraction of total volatile content in a non-aerosol sample or the non-propellant portion of an aerosol sample
A	=	Weight of empty weighing dish to the nearest 0.00001g
B	=	Weight of syringe w/ sample to the nearest 0.00001g
C	=	Weight of syringe after dispensing sample to the nearest 0.00001g
D	=	Weight of cooled weighing dish with sample residue to the nearest 0.00001g

12.2 Percent Total Volatile = TV x 100

12.3 Relative Percent Difference (RPD)

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

Where:

X = the sample result

Y = the replicate 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, August 1, 2022

13.2 U.S. EPA Method 24 Determination of Volatile Matter Content, Water Content, Volume Solids, and Weight Solids of Surface Coatings

13.3 U.S. EPA Method 24a Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings

13.4 ASTM D2369-97 Volatile Content of Coatings

13.5 NLB Laboratory Quality Control Manual, Revision 5.0, December 7, 2021

13.6 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 1.0, December 30, 2021

13.7 CARB, "Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street," November 2021 or current.

13.8 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)

13.9 SAS13 Standard Operating Procedure for Consumer Product Sample Batch Management and Reporting

13.10 SAS14 Standard Operating Procedure for Consumer Product Sample Preparation

13.11 Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Article 2, Consumer Products, Sections 94507-94517

14 Revision History

SOP/Addendum Identification	Approval Date	Description of Change
MLD SOP 300 Revision 1	October 10, 1996	Additions to the QC section the addition of the trip sample and clarify the calibration of the balance
MLD SOP ES01 Revision 2	March 10, 1998	Adjusted document font to Times New Roman 12. Inserted Appendix A formerly a stand-alone document.
MLD SOP SAS 01 Revision 3.0	October 26, 2000	Renumbered to new Section Number, Change Font to Arial 12.
MLD SOP SAS 01 Revision 1.4	June 27, 2003	Added procedure for use of Network LimsLink V2.1 software into Appendix A.

SOP/Addendum Identification	Approval Date	Description of Change
		Corrected version enumeration.
MLD SOP SAS 01 Revision 1.5	June 22, 2007	Reviewed for grammar and content. Miscellaneous additions/deletions made. Revised Appendix A to reflect use of BalanceTalk (v4.0) software instead of LimsLink v2.1 software.
MLD SOP SAS 01 Revision 1.6	August 17, 2010	Reviewed for grammar and content. Miscellaneous additions/deletions made. Added Appendix B to describe handling of atypical sample matrix.
SAS 01 Revision 1.7	October 24, 2018	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. Replaced the “Trip Sample” with “Batch Sample”. Incorporated APPENDIX A into body of SOP. APPENDIX B became APPENDIX A. Added APPENDIX B to describe handling of dryer sheets. Added additional QC: balance check after weighing.
SAS 01 Revision 2.0	December 27, 2022	Reviewed for grammar and content. Updates to QC criteria and corrective actions.

APPENDIX A

Handling of an Atypical Sample Matrix:
Viscous Oven Cleaner Containing Sodium Hydroxide and/or Entrained Propellant

1 Summary

Gravimetric results for the total weight percent VOCs can be problematic to obtain from certain sample matrices. Thick oven cleaners containing sodium hydroxide and/or entrained propellant are examples of such sample matrices. Even when using Teflon weighing dishes, the sample can forcibly eject residue during the one-hour oven drying process, and likely contaminate other nearby weighing dishes and the interior oven walls with residue. To mitigate contamination and retain the ejected residue for obtaining meaningful gravimetric results, the following handling procedures may be used.

2 Equipment and Supplies

2.1 In addition to the supplies listed in section 8 of SAS 01, the following are necessary for this appendix:

2.1.1 Teflon Petri Dish, 100mm x 15mm with a flat bottom surface

2.1.2 Teflon Bowl, 98mm x 40mm deep with 5 equally spaced approximately 1/4-inch holes drilled in the center of the bowl's bottom

3 Procedure

3.1 The Teflon Petri dish will hold a smaller Teflon weighing dish containing the sample; and the Teflon bowl will cover the sample and contain the potential ejected sample residue.

3.1.1 Place the smaller Teflon weighing dish facing up, in the middle of the large Teflon petri dish and cover with bowl (applying the sample to the smaller Teflon dish within the containment unit). This sample system of Teflon dishes and bowl comprise one sample container and containment unit.

3.2 Follow section 9 of SAS 01 using this sample system in place of a weighing dish.

APPENDIX B

Handling of an Atypical Sample Matrix: Dryer Sheets

1 Summary

This appendix describes a procedure for the measurement of the total volatile content of consumer products with VOC embedded within a delivery substrate, such as a dryer sheet, where the separation of the sample from the delivery system is not possible. The total volatile content is the difference in weight of the sample aliquot before and after heating. The total grams VOC per use is determined per the equations in Method 310, using the total volatile content of the sample aliquot as determined by this SOP.

2 Equipment and Supplies

2.1 In addition to the supplies listed in section 8 of SAS 01, the following are necessary for this appendix.

2.1.1 Weighing Dishes, 70mm w/ a smooth (planar) bottom surface

2.1.2 Scissors

2.1.3 Circular Template, 60mm diameter

3 Procedure

3.1 Begin by following sections 9.1 – 9.9 of SAS 01.

3.2 Using the circular template cut a section out of the center of the folded dryer sheet creating two sample aliquots: one sample aliquot that is circular, and one sample aliquot that is two semicircular pieces.

3.3 Place one sample aliquot into the appropriately labeled and tared weighing dish and weigh to the nearest 0.00001g. Record the weight in the column marked, “Syringe Initial Weight (g)”.

3.4 Manually enter “0” in the column marked “Syringe Final Weight (g)”.

3.5 The difference, as computed on the “Grav Calc” worksheet, is the actual amount of the product placed in the weighing dish.

3.6 Repeat this step with the second sample aliquot.

3.7 Continue following SAS 01 at section 9.12.

4 Calculations

4.1 Weight fraction of total volatile content in a non-aerosol sample or the non-propellant portion of an aerosol sample (per weighing dish)

$$TV = \left[\frac{S-(D-A)}{S}\right]$$

Where:

TV	=	Weight fraction of total volatile content in a non-aerosol sample or the non-propellant portion of an aerosol sample
S	=	Mass of the dryer sheet sample aliquot to the nearest 0.00001g
A	=	Weight of empty weighing dish to the nearest 0.00001g
D	=	Weight of cooled weighing dish with sample residue to the nearest 0.00001g